



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/IB98/00784 <b>(22) International Filing Date:</b> 20 May 1998 (20.05.98) <b>(30) Priority Data:</b> 08/864,255           28 May 1997 (28.05.97)       US 08/940,101           29 September 1997 (29.09.97)   US <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors:</b> BOLICH, Raymond, Edward, Jr.; 7201 Striker Road, Maineville, OH 45039 (US). JIVIDEN, Kathleen, Bridget; 2653 Timber Court, Lebanon, OH 45036 (US). MIDHA, Sanjeev; Apartment 2D, 9274 Deercross Parkway, Blue Ash, OH 45236 (US). MORRISSEY, Christopher, Todd; 8736 Charleston Woods Drive, Mason, OH 45040 (US). TORGERSON, Peter, Marte; 4127 U.S. Route 35 N.W., Washington Court House, OH 43160 (US). YANG, Jian, Zhong; 1-215-727, Koyo-cho Naka 2-chome, Higashinada-ku, Kobe 658 (JP). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HAIRSPRAY COMPOSITIONS CONTAINING SILICONE BLOCK COPOLYMERS		
<b>(57) Abstract</b> <p>The present invention relates to hairspray compositions comprising from about 50 % to about 99.9 % by weight of an alcohol solvent, and from about 0.1 % to about 30 % by weight of a silicone-containing adhesive block copolymer having a weight average molecular weight from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with select silicone macroinitiators, preferably silicone macroazoinitiators. The hairspray compositions, when dried, preferably have a cohesive strength of greater than about 0.5 kgf/mm<sup>2</sup>, a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm<sup>3</sup>, an impact strength of greater than about 7000 ergs, and an improved removeability from hair as defined by a hair stiffness value of from 0 to about 3.5 (0 to 4 scale) and a hair flaking value of from 0 to about 3.5 (0 to 4 scale). These hairspray compositions provide improved hair styling performance, and in particular provide improved maintenance or hold when applied to dry hair and causes minimal or no drooping of the hair during or immediately after application.</p>		

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## HAIRSPRAY COMPOSITIONS CONTAINING SILICONE BLOCK COPOLYMERS

### TECHNICAL FIELD

The present invention relates to hairspray compositions which provide improved hair style retention characteristics and hair feel. These compositions comprise a silicone-containing adhesive block polymer and at least about 50% by weight of an alcohol solvent.

### BACKGROUND OF THE INVENTION

Hair styling compositions are well known and include compositions formulated for and intended for application as shampoos, hairsprays, aerosol mousses, and other formulations known for use in delivering hair styling polymers to the hair. These compositions are typically applied to wet or dry hair, depending on the formulation, and allowed to form thin hair styling films or welds to the applied surface.

Hair styling compositions are commonly formulated as hairsprays intended for application to dry, positioned or styled hair to maintain or hold the position of such dry, styled hair. These hairsprays are typically applied to the hair as pump sprays or from pressurized aerosol canisters. Such compositions provide temporary setting benefits to dry, styled hair and can usually be removed by water or by the next shampooing. The hair styling materials used in hairspray compositions are generally in the form of resins, gums, and adhesive polymers.

Many hairsprays, however, tend to deposit hair styling material on the hair that leaves the hair either excessively stiff or excessively sticky after the material has been applied to the hair and allowed to dry. Excessively stiff hairsprays are brittle and break down under common stresses such as wind, brushing, combing, and often feel or look unnatural. On the other extreme, excessively sticky hairsprays are more flexible under stress and are not excessively brittle, but leave the hair with a heavy, coated feel and a limp appearance as the hair droops and does not readily maintain or hold the intended style of the hair. These excessively sticky hairsprays also cause the hair to quickly become soiled from dust, dirt, lint, sebum, and other common contaminants that more readily adhere to the sticky hairsprays.

Some hairsprays have been formulated which can be applied to clean, dry hair to maintain or hold the desired hair style, and which are neither excessively stiff

or sticky after application. However, many of these hairsprays still cause the hair to droop excessively immediately after application to the dry, styled or positioned hair. The applied hairspray then solidifies on the hair, and then retains the drooped or otherwise limper position of the hair caused by the initial application of the hairspray.

It has now been found that the hairspray compositions of the present invention are especially effective in providing hair styling performance when applied to dry, styled or positioned hair, without causing the hair to be excessively stiff or sticky and without causing the hair to excessively droop immediately after application. These hairspray compositions comprise select silicone-containing adhesive copolymers in combination with an alcohol solvent, wherein the composition contains at least about 50% by weight of the alcohol solvent. The hairspray compositions when dried preferably have a cohesive strength of greater than about  $0.5 \text{ kgf/mm}^2$ , a total energy absorption per unit volume of greater than about  $0.55 \text{ kgfmm/mm}^3$ , and an impact strength of greater than about 7000 ergs.

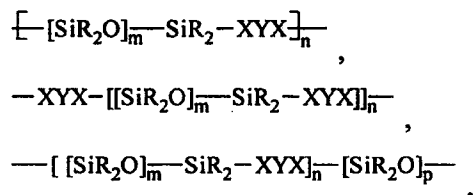
It has also been found that the preferred hair spray compositions of the present invention have an improved removeability from hair during shampooing, wherein the removeability is defined in terms of hair stiffness and hair flaking values ranging from 0 to about 3.5 (0 to 4 scale). These hair stiffness and flaking values are indirect measures of hair spray removeability. Each of these values are determined in accordance with the methodology defined herein.

It is therefore an object of the present invention to provide hairspray compositions that are neither excessively sticky nor excessively stiff after application, and further to provide such a composition that causes minimal or no drooping of dry, styled or positioned hair after application, and further to provide a hairspray composition having an improved removeability as defined herein. It is yet another object of the present invention to provide such a composition which comprises select silicone-containing block polymers in combination with high concentrations of an alcohol solvent, and further to provide a method of styling dry, styled or positioned hair without causing excessive drooping of the dry hair immediately after application and without causing the hair to feel excessively stiff or sticky.

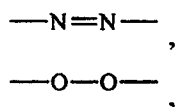
#### SUMMARY OF THE INVENTION

The present invention relates to hairspray compositions comprising from about 50% to about 99.9% by weight of an alcohol solvent, from about 0.1% to about 30% by weight of a silicone-containing adhesive block polymer having a

weight average molecular weight of from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with a silicone macroinitiator, wherein the silicone macroinitiator contains a chemical group selected from the group consisting of



and combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof; X is a divalent radical; Y is selected from the group consisting of



and combinations thereof; m, n, and p are positive integers each independently having a value of 1 or greater.; and wherein the silicone macroinitiator has a number average molecular weight from about 500 grams/mole to about 500,000 grams/mole, and wherein the hairspray composition, when dried, preferably has a cohesive strength of greater than about 0.5 kgf/mm<sup>2</sup>, a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm<sup>3</sup>, and an impact strength of greater than about 7000 ergs. The hair spray compositions preferably have improved removeability, wherein improved removeability is defined by a hair stiffness value of from 0 to about 3.5 and a hair flaking value of from 0 to 3.5 (0 to 4 scale)

It has been found that these hairspray compositions are especially effective in providing hair styling performance when applied to dry, styled or positioned hair. In particular, these hairspray compositions can be applied to dry, styled or positioned hair without causing the hair to be excessively stiff or sticky after the hairspray has dried onto the hair, and without causing the dry, styled or positioned hair to excessively droop immediately after application of the hairspray composition and before the applied composition solidifies and sets onto the hair.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an overhead view of a dumbbell-shaped planar dried hairspray film sample useful for measuring the physical properties such as the cohesive strength and total energy absorption per unit volume as described herein.

Fig. 2 illustrates a cross-sectional view, showing the thickness of the dumbbell-shaped dried film illustrated in Fig. 1.

### DETAILED DESCRIPTION OF THE INVENTION

The hairspray compositions of the present invention comprise select silicone-containing adhesive block polymers in combination with an alcohol solvent. Each of these essential components, as well as preferred or optional components, are described in detail hereinafter.

All percentages, parts and ratios are by weight of the total referenced composition, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include solvents or by-products that may be included in commercially available materials, unless otherwise specified.

All molecular weights as used herein are weight average molecular weights expressed as grams/mole, unless otherwise specified.

The term "suitable for application to human hair" as used herein, means that the compositions or components thereof so described are suitable for use in contact with human hair and the scalp and skin without undue toxicity, incompatibility, instability, allergic response, and the like.

The term "adhesive" as used herein refers to the silicone-containing block copolymers in the hairspray composition of the present invention that when applied as a solution or dispersion to a surface and dried, e.g., the hair fibers, the block copolymer forms films or welds onto the applied surface. Such a film or weld will have adhesive and cohesive strength, as is understood by those skilled in the art.

The term "kgf" as used herein is a unit of measure characterized as kilogram of force subjected to gravitational acceleration, i.e.  $9.82 \text{ m/s}^2$ .

The hairspray compositions of the present invention can comprise, consist of, or consist essentially of the essential elements of the invention described herein, as well as any of the additional or optional ingredients, components, or other limitations described herein.

#### Alcohol solvent

The hairspray compositions of the present invention comprise an alcohol solvent that dissolves or disperses the silicone-containing block copolymer described in detail hereinafter. Concentrations of the alcohol solvent ranges from about 50%

to about 99.9%, preferably from about 50% to about 90%, more preferably from about 55% to about 80%, by weight of the hairspray compositions.

Alcohol solvents suitable for use in the hairspray compositions of the present invention are preferably ethanol, n-propanol, isopropanol, and combinations, wherein the selected silicone-containing adhesive block polymer is soluble in the selected alcohol solvent at a concentration of at least about 0.1 mg/mL, preferably at least about 0.5 mg/mL, and more preferably at least about 1 mg/mL, at about 22.7°C.

The hairspray composition may further comprise other additional solvents, including water, provided that the silicone-containing block copolymer remains dissolved or otherwise dispersed in the hairspray composition, and provided that such additional solvents are chemically and physically compatible with the ingredients of the composition and that it does not substantially and unduly impair product performance. The hairspray compositions may further comprise up to about 45% by weight of water, preferably less than about 40%.

It has been found that the alcohol solvent, at the above-described concentrations, when used in combination with the select silicone-containing adhesive block polymers is especially effective at providing improved hair styling performance to the hairspray composition of the present invention. This combination of select polymers and alcohol solvents is even more effective in minimizing or eliminating the undesirable drooping of dry, styled or positioned hair immediately after application to the hair.

#### **Adhesive Block Copolymer**

The hairspray composition of the present invention comprises select silicone-containing adhesive block copolymers as defined herein, which help provide the improved hair styling performance to the composition, and which are soluble or dispersible in the alcohol solvent of the hairspray composition. Concentrations of the block copolymers in the hairspray composition ranges from about 0.1% to about 30%, preferably from about 0.5% to about 20%, and more preferably from about 0.5% to about 10%, by weight of the composition.

The silicone-containing adhesive block copolymers selected for use in the hairspray compositions of the present invention are prepared by the free radical polymerization of select silicone containing macroinitiators (described in detail hereinafter) and ethylenically unsaturated monomers. The resulting block copolymers comprise sequentially arranged moieties or blocks which are further composed of smaller repeating units. The silicone-containing adhesive block

copolymers herein comprise silicone-containing blocks derived from silicone-containing macroinitiators (hereinafter Block A) and other blocks derived from ethylenically unsaturated monomers as defined herein (hereinafter Block B). These block copolymers are either A-B block structures containing two block segments; A-B-A block structures containing three block segments,  $-(A-B)_n-$  block structures containing multiple blocks wherein  $n$  is an integer having a value of 2 or more, or combinations thereof.

The hairspray compositions of the present invention comprises any one of the of the block structures described above, including mixtures or combinations thereof, and also including combinations thereof with small amounts of unreacted monomer or small amounts of homopolymers derived from the ethylenically unsaturated monomers described herein or the silicone-containing macroinitiators also described herein.

The silicone-containing adhesive block copolymers herein have a weight average molecular weight of from about 10,000 grams/mole to about 10,000,000 grams/mole, preferably from about 20,000 grams/mole to about 1,000,000 grams/mole, more preferably from about 30,000 grams/mole to about 1,000,000 grams/mole, even more preferably from about 60,000 grams/mole to about 750,000 grams/mole, and most preferably from about 70,000 grams/mole and about 750,000 grams/mole.

The silicone-containing adhesive block copolymers for use in the hairspray compositions herein are prepared by free radical polymerization of ethylenically unsaturated monomers and the silicone-containing macroinitiators described herein. Polymerization reactions of this type are generally well known in the polymer art, some descriptions of which are disclosed by M. Mishra, *Macromolecular Design: Concept and Practice*, Polymer Frontiers International, Inc., pages 313-358 (1994); European Patent Application 766957A1, published April 9, 1997; and Odian, *Principles of Polymerization*, 3rd edition, John Wiley & Sons, pages 198-334 (1991), which descriptions are incorporated herein by reference in their entirety.

The free radical polymerization reaction referenced herein can be accomplished, for example, by combining the ethylenically unsaturated monomer and the polysiloxane macroinitiator in a reactor along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The reaction is brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can



be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The resulting block copolymer can be further purified, as desired, and used in formulating the hairspray composition of the present invention by formulation techniques well known in the art.

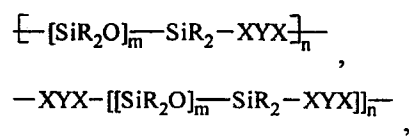
The silicone-containing adhesive block copolymers for use herein can also be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

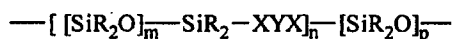
Other examples of silicone-containing block copolymers and methods of making them are described in U.S. Patent 5,523,365, to Geck et al., issued June 4, 1996; U.S. Patent 4,689,289, to Crivello, issued August 25, 1987; U.S. Patent 4,584,356, to Crivello, issued April 22, 1986; Macromolecular Design, Concept & Practice, Ed: M.K. Mishra, Polymer Frontiers International, Inc., Hopewell Jct., NY (1994); and Block Copolymers, A. Noshay and J.E. McGrath, Academic Press, NY (1977), which descriptions are incorporated herein by reference.

#### Silicone-containing Macroinitiator

The silicone-containing adhesive block copolymers of the hairspray composition herein comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of silicone-containing blocks, wherein the silicone-containing blocks are derived from the select silicone-containing macroinitiators described herein.

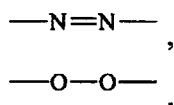
The silicone-containing macroinitiator for use in the hairspray composition of the present invention is selected from the group consisting of the following formulas:





or combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof, preferably methyl group; each X is a divalent linking group which may be the same or different for any given silicone-containing macroazoinitiator, and which may include the following groups: acyl, alkyl, aryl, amide, alkene, alkyne, ether, ester, sulfone, sulfoxide, thioether, halogen, nitrile and combinations thereof, preferably amide or ester groups for ease of synthesis. Other divalent linking groups can also be used provided that they do not substantially and unduly impair the free radical polymerization reactions described herein.

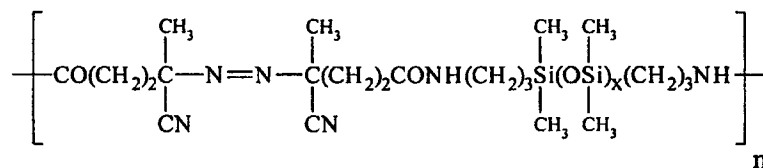
In the above described macroinitiator formulas, each Y is independently selected from the group consisting of those chemical moieties represented by the following formulas:



or combinations thereof; each of m, n, and p value are positive integers each independently having a value of 1 or greater, preferably m and p have values independently from about 14 to about 700, whereas n has no upper value except that it should not be so large as to limit applicability for practical reasons (viscosity, processing, solvent compatibility, etc.) during the polymerization reaction of the silicone-containing adhesive block copolymers, but is preferably a value of from about 1 to about 10.

The number average molecular weight of silicone-containing macroinitiator is from about 500 grams/mole to about 500,000 grams/mole, preferably from about 2,000 grams/mole to about 250,000 grams/mole, more preferably from about 5,000 grams/mole to about 100,000 grams/mole.

Preferred are the silicone-containing macroinitiators wherein Y is an azo group, even more preferably those silicone-containing macroazoinitiators corresponding to the following formula:



wherein x is an integer having a value of from about 50 to about 150, and n is an integer having a value of from about 4 to about 12, more preferably from about 6 to

about 9. Most preferred are those macroazoinitiators represented by the above formula wherein  $x$  is an integer having a value of either about 135 or 67, and  $n$  is an integer having a value of from about 6 to about 9.

The silicone-containing blocks (Block A) of the block copolymers herein preferably contain at least about 10 repeating monomer units, more preferably at least about 40 monomer units, even more preferably at least about 60 monomer units, wherein each of the repeating monomer units are derived from the select silicone-containing macroinitiators described herein, and the average molecular weight of each silicone-containing block preferably ranges from about 500 grams/mole to about 60,000 grams/mole, more preferably from about 1,000 grams/mole to about 25,000 grams/mole, even more preferably from about 2,000 grams/mole to about 15,000 grams/mole.

#### Ethylenically Unsaturated Monomer

The silicone-containing adhesive block copolymers of the hairspray composition herein comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90%, by weight of a copolymerizable ethylenically unsaturated monomers.

The blocks (block B) in the silicone-containing adhesive block copolymer are derived from ethylenically unsaturated monomers, wherein block B has a glass transition temperature ( $T_g$  value) of more than about  $-20^{\circ}\text{C}$ , more preferably more than about  $-5^{\circ}\text{C}$ , and also preferably less than about  $60^{\circ}\text{C}$ , more preferably less than about  $50^{\circ}\text{C}$ , and even more preferably less than about  $40^{\circ}\text{C}$ .

The ethylenically unsaturated monomers are copolymerizable with the silicone-containing macroinitiators and contain at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted. Preferred are vinyl monomers. Either a single type of ethylenically unsaturated monomer or combination of two or more ethylenically unsaturated monomers can be used. The ethylenically unsaturated monomers are selected to meet the requirements of or preferences for the silicone-containing adhesive block copolymers described herein, including solubility in the selected alcohol solvent, glass transition temperatures within the above-described ranges for hair styling or conditioning performance, reactivity with the selected silicone-containing macroinitiator, and so forth.

The ethylenically unsaturated monomers for use in making the silicone-containing adhesive block copolymers may be hydrophilic or hydrophobic, water soluble or water insoluble. These ethylenically unsaturated monomers are preferably hydrophilic monomers, or combinations of hydrophilic and hydrophobic monomers

provided that the resulting block copolymer in the hairspray composition has the requisite solubility and other characteristics defined herein. The term "hydrophilic monomers" as used herein refers to monomers which form water soluble homopolymers, whereas the term "hydrophobic monomers" as used herein refers to monomers which form water-insoluble polymers. In this context, the term "water soluble" means that the polymer is soluble in water, ethanol, n-propanol, isopropanol, or combinations thereof, at a concentration of at least about 0.1mg/ml, preferably at a concentration of at least about 0.5mg/ml, even more preferably at a concentration of at least about 1mg/ml, at 22.7°C.

The ethylenically unsaturated monomers when copolymerized into repeating units or blocks (block B) in the silicone-containing adhesive block copolymer herein preferably contains at least about 10 repeating monomers, more preferably at least about 20 repeating monomers, even more preferably at least about 50 repeating monomer units.

Nonlimiting classes of ethylenically unsaturated monomers useful herein include unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and combinations thereof.

Some examples of suitable ethylenically unsaturated monomers include, but are not limited to, acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, acrylic and methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol,

methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols preferably having from about 1 to about 12 carbon atoms; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamentyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxylmethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene;  $\beta$ -pinene;  $\alpha$ -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the free radical copolymerization reaction with the macroinitiator described hereinafter.

Preferred ethylenically unsaturated monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.

#### Neutralized Block Copolymers

The silicone-containing adhesive block copolymers may comprise acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility or dispensability of the block copolymer in the alcohol solvent defined herein. In addition, use of the neutralized form aids in the ability of the hair styling spray compositions to be removed from the hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about

40% to about 85%, neutralization of the acidic functionalities of the silicone-containing adhesive block copolymer.

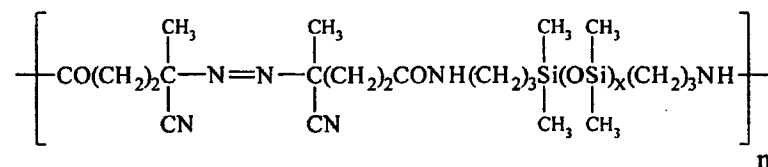
Neutralization of the silicone-containing adhesive block copolymer containing acidic functionalities may be accomplished by any conventional or otherwise known technique for affecting such neutralization by using an organic or inorganic base material. Metallic bases are particularly useful for this purpose. Suitable base neutralizers include, but are not limited to, ammonium hydroxides, alkali metal hydroxides, or an alkaline earth metal hydroxides, preferably potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents include, but are not limited to, amines or amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS) and combinations thereof. Preferred are amines and metallic bases.

Neutralization of silicone-containing adhesive block copolymer containing basic functionalities, e.g., amino groups, are likewise preferably at least partially neutralized with an organic or inorganic acid e.g., hydrogen chloride. Neutralization can be accomplished by any conventional or otherwise known technique for accomplishing such neutralization. The preferred extent of neutralization is the same as that described for neutralization of acidic functionalities.

Solubility of the selected silicone-containing adhesive block copolymer, if the selected copolymer contains an acidic or basic functionality, should be determined after the desired acid or base neutralization.

#### Preferred Silicone-Containing Adhesive Block Copolymers

Nonlimiting examples of preferred silicone-containing adhesive block polymers include, but are not limited to, the following block copolymers derived from the macroazoinitiators which conform to the following formula.



[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)]<sub>n</sub>

t-butyl acrylate: 40%; n-butyl acrylate: 28%; acrylic acid: 12%; methacrylic acid: 10%;

silicone macroazoinitiator (above-described formula,  $x=135$ ,  $n$  is from about 6 to about 9) 10%;

Molecular weight of silicone block: 10,000 grams/mole

Polymer molecular weight: 114,000 grams/mole.

[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-acrylic acid)] $_n$

t-butyl acrylate: 40%; n-butyl acrylate: 24%; acrylic acid: 21%;

silicone macroazoinitiator (above-described formula,  $x=135$ ,  $n$  is from about 6 to about 9) 15%;

Molecular weight of silicone block: 10,000 grams/mole.

Polymer molecular weight: 86,000 grams/mole.

[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-ethyl acrylate-co-acrylic acid)] $_n$

t-butyl acrylate: 32%; ethyl acrylate: 33%; acrylic acid: 20%;

silicone macroazoinitiator (above-described formula,  $x=67$ ,  $n$  is from about 6-9) 15%.

Polymer molecular weight: 110,600 grams/mole.

Molecular weight of silicone block: 5000 grams/mole.

The preferred silicone-containing macroazoinitiators described above are available from Wako Chemical USA, Inc., Richmond, Virginia, USA as VPS1001 and VPS 0501 (poly(dimethylsiloxane) initiators).

### **Properties of the Dried Hairspray Compositions**

The hairspray compositions of the present invention, when dried, preferably have specific physical properties as defined by cohesive strength, total energy absorption per unit area, impact strength and improved removeability (defined in terms of hair stiffness and flaking values). Each of these preferred physical properties is described in detail hereinafter.

#### **Cohesive Strength (kgf/mm<sup>2</sup>)**

Cohesion is the strength of the bonds formed within a sample, e.g., a dried hairspray composition. The cohesive strength, which is designated as kgf/mm<sup>2</sup> (kilograms of force per square millimeter) is the maximum unit stress a material will

withstand when being subjected to displacement in tension. Stress is the ratio of measured load (kg X f) to the original cross-sectional area ( $\text{mm}^2$ ) of the sample.

The cohesive strength of dried hairspray compositions of the current invention are determined using the following method. This method is based on ASTM Designation: D 638-91, Standard Test Method for Tensile Properties of Plastics, Published January 1992, herein incorporated by reference in its entirety. The following test method to measure cohesive strength is similar to the ASTM standard, however, several modifications are made to better represent the tensile properties of the dried hairspray films. The measurements are made at about 22.7°C and about 50% relative humidity. The test method, described herein specifically uses a modified dumbbell shape with a thickness equal to about 0.4 mm., and uses an Instron Model Mini-55 (available from Instron Corp., Canton, MA) as the testing machine for applying the force to the polymer film samples.

A dried film sample is prepared by drying an amount of the hairspray composition (i.e., the silicone-containing adhesive copolymer and solvent selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, and any additional optional components) in a flat-bottomed aluminum mold coated with PFA (perfluoroalkoxy) Teflon®. The copolymer film is dried at about 22.7°C and about 50% relative humidity until film has attained a "constant weight". By "constant weight" is meant that there is less than a 1% weight fluctuation in the sample over a period of 24 hours. The drying film should be kept in an area protected from air currents, which could result in non-uniform drying and formation of air bubbles. The copolymer film is cut into a dumbbell shape for testing. The sample should be substantially free of defects, i.e. cracks, chips, tears, etc. Figures 1 and 2 illustrate the planar dumbbell shaped film to be used in the tensile testing described herein for the cohesive strength and the total energy absorption per unit volume. Figure 1 illustrates an overhead view of the dumbbell shaped sample. Figure 2 illustrates a cross section through the dumbbell shaped sample. The width of the narrow section, 1, of the dumbbell is about 3 mm (1 = 3 mm). The length of the narrow, 3 mm., section of the dumbbell, 3, is about 13 mm. (3 = 13 mm.). The gauge length of the narrow section, 2, is the initial film length used in the determination of the strain of the sample. The gauge length is equal to or less than the length of the narrow section, preferably equal to the length of the narrow section (i.e., 2 = 3). The width of the ends of the dumbbell, 4, are about 10 mm. (4 = 10 mm.). The distance between end sections of the film, 5, is about 28 mm. (5 = 28 mm.). The overall length of the film, 6, is about 64 mm. (6 = 64 mm.). The length of the wide ends of the film is about 18 mm. ( $(6-5)/2 = 18 \text{ mm.}$ ). The transition



sections between the wide ends and the narrow section of the film are about 6.5 mm. in length (i.e.  $(5-3)/2 = 6.5$  mm.). Also the end portions of the narrow, center portion should be smoothly curved to avoid any stress points in the sample. The curve of the transition section, should have a radius,  $r$ , of from about 0.5 in. to about 5 inches, and should join tangentially to the narrow section. The film is formed to a thickness,  $t$ , of 0.4 mm. ( $t = 0.4$  mm.). The dumbbell shaped samples are further equilibrated to a "constant weight". By "constant weight" is meant that over a selected 4 day period, there is no more than 0.2% average weight gain or loss, relative to the dumbbell's measured weight 4 days previous and no more than  $\pm 0.2\%$  weight drift should be observed between two consecutive measurements in the four day period of time. The dumbbell should be tested within a 7 day period of reaching this constant weight.

The samples are tested on a calibrated Instron Model Mini-55 tensile tester. Before mounting the sample into the Instron, the length,  $L$ , width,  $W$ , and thickness,  $t$ , of the narrow section of the dumbbell shaped sample are measured to the nearest micron with a calibrated micrometer. The dimensional measurements are required by the Instron for force per unit area calculations. The wide ends of the dumbbell samples are clamped into the Instron and pulled at a crosshead rate of 5 mm. per minute. The Instron tester measures the overall forces (e.g., kgf) applied to the film. These forces are spread over the cross sectional area of the narrow section of the film. The cohesive strength of the copolymer is the maximum unit force measured by the Instron divided by the cross sectional area of the narrow portion of the film.

The dried hairspray compositions of the present invention have a cohesive strength of greater than about  $0.5 \text{ kgf/mm}^2$ , preferably greater than about  $0.6 \text{ kgf/mm}^2$ , and more preferably greater than about  $0.7 \text{ kgf/mm}^2$ .

#### Total Energy Absorption Per Unit Volume (e.g., $\text{kgfmm/mm}^3$ )

The total energy absorption per unit volume, which is designated as  $\text{kgfmm/mm}^3$  (kilograms of force millimeters per millimeter cubed), is the ratio of the total energy required to reach the autobreak point (in  $\text{kgf} \times \text{mm}$ ) to the original volume of the sample ( $\text{mm}^3$ ). The total energy required to reach the break point is calculated using standard techniques by determining the area under a load versus displacement curve for the sample. The total energy absorption per unit volume is also known as "toughness" by those skilled in the art of polymer science and materials testing.

The measurements are made at about  $22.7^\circ\text{C}$  and about 50% relative humidity.

The dried hairspray compositions of the present invention preferably have a total energy absorption per unit volume of greater than about  $0.55 \text{ kgfmm/mm}^3$ ,

more preferably greater than about 0.75 kgfmm/mm<sup>3</sup>, even more preferably greater than about 1.10 kgfmm/mm<sup>3</sup>, and most preferably greater than about 2.15 kgfmm/mm<sup>3</sup>.

### **Impact Strength**

Impact strength is the mean-failure energy (mass X gravity X height) required to produce sample failure, e.g., in a dried hairspray composition. The sample failure is characterized by a crack or split created by the impact of the falling weight that can be seen by the naked eye under normal laboratory lighting conditions.

The impact strength of the dried hairspray compositions of the current invention are determined using the following method. This method is based on ASTM Designation: D 5420-93, Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact), Published 1995, herein incorporated by reference in its entirety, however, several modifications are made to better represent the impact properties of the dried film. The measurements are made at about 22.7° C and about 50% relative humidity.

The test method, described herein specifically uses rectangular shaped samples with a thickness equal to about 0.4 mm, and uses a GCA/Precision Scientific Penetrometer modified to drop a blunt faced probe to a distance of 70 mm and equipped with a Precision Scientific solenoid controller for GCA Penetrometer, a blunt faced cylindrical probe with a surface area of 8 mm<sup>2</sup> (OK M&T Corp. - part # WSU30), and a ruler which measures in 1 mm increments.

The samples are prepared using the film drying method described above in the cohesive strength measurements. The copolymer film is cut into the rectangular shape, e.g. 10 mm X 20 mm. The thickness of the sample is 0.4 mm. The film thickness of various test samples should be maintained within ±15% of 0.4 mm.

The following measurement process is used. Turn on the solenoid operated probe release controller. The controller should begin to cycle on and off as indicated by a red light. Be sure the probe face is flush with the impact surface so that the sharp edge of the probe does not strike the film. Place a film sample on the Impact Tester over the target area. Direct the metric ruler gently on the film sample. Direct the lightening source across the surface of the sample such that the light source is in the same plane as the surface of the film. Small fractures in the film will reflect light and be easily detected. Move the probe up to desired drop distance. A suggested distance progression is: 1 mm, 3 mm, 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, and further 5 mm increments up to 70 mm. (70 mm is the upper limit of the instrument).

Turn on the instrument switch, to drop the probe onto the sample. The first step in the measurement of impact energy is to find the range of probe height necessary to fracture the film. Start at 1 mm for the first step. Continue to move up according to the suggested distance progression until a fracture is observed. When a fracture is observed make a note of it and move to a new sample. The second step in determining impact energy is to set a new sample and start drop at an observed fracture point in the range procedure. Set a new film sample and move the probe to the next lowest setting. If the film fractures, record result and repeat previous step. If the film does not fracture, set a new sample and move to the next distance. Continue to set new samples and increase the drop distance until the film fractures. Continue the procedure until 5 fractures are observed. Calculate the amount of work energy, i.e. the fracture strength using the following formula:

$W = m \times g \times h$ , where

W = amount of work energy in ergs,

m = mass of probe (59.53 g) (The probe is removable and can be replaced with one of different mass or impact surface area).

g = gravitational constant (980.665 cm/sec<sup>2</sup>),

h = average distance probe travels to impact (cm).

The dried hairspray compositions of the present invention preferably have an impact strength of greater than about 7000 ergs, more preferably greater than about 20,000 ergs, and even more preferably greater than about 50,000 ergs.

### **Hair Spray Removeability**

The adhesive copolymers herein have improved removeability when used in the preferred hairspray embodiments of the present invention. In this context, improved removeability means that the adhesive copolymers are more easily removed from the hair or other applied surface during shampooing.

For purposes of defining the preferred hair spray compositions of the present invention, removeability is determined indirectly by evaluating hair stiffness and the appearance of observable white flakes after treating the hair in accordance with the removeability methodology described hereinafter. It has been found that the removeability of a hair spray formulation after shampooing correlates with the resulting stiffness/softness of the hair and the appearance/nonappearance of white flakes on the hair after a series of shampooing cycles. The hair spray compositions of the present invention have high removeability e.g., reduced stiffness and reduced white flaking. The term "removeability" as used herein therefore refers to hair

stiffness values (0-4 scale) and white flaking values (0-4 scale) as measured in accordance with the methodology described hereinafter.

For purposes of the defining the preferred hair spray compositions of the present invention, the removeability of the hair spray compositions is defined as a combination of hair stiffness values and hair flaking values, wherein the hair spray compositions provide hair flaking values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0, and hair stiffness values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0.

#### **Methodology: Hairspray Removeability**

Removeability of the hairspray composition of the present invention, as indirectly evaluated in terms of hair stiffness and the appearance of white flakes, is determined in accordance with the following methodology. The methodology simulates multiple application and multi-cycle application of hairspray compositions so as to indirectly determine how readily and effectively such hairspray compositions are removed from hair.

The methodology described herein provides a means of evaluating hair switches blindly treated with hairspray embodiments of the present invention. The method by which each hair switch is treated with the hairspray embodiments, and the method by which each treated hair switch is then evaluated for removeability are described in detail below.

Two trained panelists each evaluate identically treated hair switches or sets of hair switches for stiffness and the appearance of white flakes. The panelists then individually assign each of the treated hair switches with a numerical score (0 to 4 scale) for hair stiffness and a numerical score for flaking (0 to 4 scale). The order in which the hair switches are treated with different hair spray embodiments is randomized and conducted round robin. Two identical sets of switches are prepared as described below for each panelist so that each has a fresh set of switches to evaluate. Before evaluating the blindly treated hair switches, each panelist also evaluates (not blinded) an untreated hair switch as a zero reference for hair stiffness and flaking. Each panelist also evaluates a control treated hair switch as a flaking reference (score 4.0) and another control treated hair switch as a hair stiffness reference (score 4.0). The hair stiffness values as defined herein are determined by averaging the hair stiffness scores provided by the two panelist. Likewise, the hair flaking values as defined herein are determined by averaging the hair flaking scores provided by the two panelists.

The hair switches are treated with either an aerosol or non-aerosol hair spray embodiment of the present invention in accordance with the following steps. The hair stiffness reference and the flaking reference are also prepared in accordance with the following steps, except that each is treated with the corresponding hair spray formulations as described hereinafter in Tables 2 and 3.

- 1) Vertically suspend a clean hair switch (10 inch European virgin brown hair, 20 gram) from its bound end and comb (black rubber comb, 5 inches by 1 inch, 1/2 fine tooth) through the switch to remove any tangles.
- 2) If necessary, use a static gun to eliminate any static build-up on the switch.
- 3) For non-aerosol products, spray the switch from a distance of 4 inches while applying ten pumps of the product to the switch and while moving the atomized spray pattern in a fluid up-and-down motion to cover the entire switch, or for aerosol products, spray each switch from a distance of 6 inches while applying the aerosol stream to the switch for a period of 3 seconds and while moving the aerosol stream in a fluid up-and-down motion to cover the entire switch.
- 4) Repeat step 3 on the opposite side of the switch.
- 5) After spraying the opposite side of the switch, hang the treated switch from its bound end to allow it to dry for one hour at ambient temperature, pressure and humidity.
- 6) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 7) Repeat steps 1 through 6.
- 8) Wet the treated hair switch with water (+15-20 grain hardness, 38°C, 1 gal/min. water pressure).
- 9) Apply 1 ml of shampoo (Table 1: methodology shampoo) along the length of the front of the wet hair switch and apply another 1 ml of the shampoo along the length of the reverse side of the wet hair switch.
- 10) Gently milk the switch from top to bottom (hand over hand between thumb and fingers) for 15 seconds at 1 stroke per second.
- 11) Rinse the hair switch with water (38°C, +15-20 grain hardness, 1 gal/min. water pressure) for 15 seconds. Gently squeeze the hair between the first and

second fingers, drawing the fingers down the switch after 5 seconds, 10 seconds, and after final rinse.

- 12) Hang the treated switch and allow it to dry for two hours at 60°C in a hot box.
- 13) Remove the dried switches from the hot box.
- 14) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 15) Repeat steps 1-14.
- 16) Repeat steps 1-13.
- 17) A panelist then evaluates the treated switch by feeling it between their first and second fingers of their dominant hand and between their thumb and other fingers for stiffness and resistance to bending, and then assigns to the treated switch a hair stiffness score (0 to 4 scale). The value of the assigned score is relative to the hair stiffness reference score (4) and the untreated reference score (0).
- 18) The panelist then combs the evaluated switch in accordance with the procedure set forth in Step 14 above, and then visually evaluates the combed switch for white flakes, coating, and white haze and assigns it a hair flaking score (0 to 4 scale). The value of the assigned score is relative to the hair flaking reference score (4) and the untreated reference score (0).

Table 1: Methodology Shampoo

Ingredient List	Percent Composition As Added	Percent Composition Chemical Content
Sodium Laureth Sulfate	40.0000	10.0000
Water - USP Purified	30.3000	30.3000
Sodium Lauryl Sulfate	29.1000	8.0025
Cocamide DEA	.5000	.4000
Kathon CG	.1000	.0015
Citric Acid Solution (50% active)	** adj. from 0 - 1% (note: water level qs. to 100%)	

Table 2: High Flaking Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	4.50	4.50
Water - USP Purified	15.50	15.50
Ethanol (SDA 40)	80.00	80.00

Table 3: High Stiffness Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	6.00	6.00
Aminomethylpropanol, 95%	1.04	0.99
Water - USP Purified	15.50	15.50
Diisobutyl Adipate	0.20	0.20
Ethanol (SDA 40)	80.00	80.00

Each of the formulations described in Tables 1-3 are prepared by conventional formulation and mixing techniques.

### **Optional Ingredients**

The hairspray compositions of the present invention may further comprise one or more optional ingredients known or otherwise effective for use in hairsprays and other hair styling compositions. These optional ingredients may be used to improve or otherwise modify aesthetics, performance or stability of the hairspray compositions. Concentrations of such optional ingredients will vary with the type of material added and its intended performance, but will typically and collectively range from about 0.005% to about 50%, more typically from about 0.05% to about 30% by weight of the composition.

Plasticizers for the silicone-containing adhesive block copolymer are especially useful in the hairspray herein. Suitable plasticizers include any known or otherwise effective plasticizer suitable for use in hair care or other personal care compositions, nonlimiting examples of which include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C<sub>2</sub>-C<sub>8</sub> alkyl citrates, including triethyl citrate

and tri-propyl, -butyl, -pentyl, etc., analogs of triethyl citrate, and combinations thereof. Preferred is triethyl citrate.

Plasticizers are typically used at concentrations of from about 0.01% to about 10%, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%, by weight of the hairspray composition. Preferably, the weight ratio of silicone-containing block copolymer to the plasticizer is from about 1:1 to about 40:1, preferably from about 2:1 to about 30:1, more preferably from about 3:1 to about 25:1.

Other optional ingredients include an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hairspray composition. Preferred are minimum concentrations of at least about 0.01% by weight of the hairspray composition, and maximum concentrations sufficiently low for the selected system that the silicone-containing adhesive block copolymer remains solubilized or otherwise dispersed in the hairspray composition. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the solubility of the silicone-containing adhesive block copolymer in the hairspray composition will decrease until it is no longer soluble or dispersible in the composition and will precipitate out of the composition. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifier, alcohol solvent, other liquid vehicles, block copolymer, and other ingredients present in the composition. Concentrations of the optional ionic strength modifier are typically range from about 0.01% to about 4%, preferably from about 0.01% to about 2%, more preferably from about 0.01% to about 0.1%, by weight of the composition

The optional ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm<sup>2</sup>. Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The optional ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH<sup>-</sup> and H<sup>+</sup> do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the



composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the hairspray composition. The ionic strength modifiers can be incorporated into the hairspray compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. When such an optional ionic strength modifier system is used, it is a necessary that both anions and cations of the optional ionic strength modifier system be included in the hairspray composition.

Nonlimiting examples of suitable optional cations for use in the compositions are alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, more preferably sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below. Other nonlimiting examples of suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

Other optional ingredients include surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene

cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

#### Hairspray Products

The hairspray compositions of the present invention are dispensed as sprayed or atomized liquids from any container or package known or otherwise effective for providing such delivery. Such containers or packages will typically be in the form of pump spray dispensers or aerosol canisters, both of which are well known to those skilled in the art.

The hairspray compositions of the present invention further comprises a propellant when dispensed from a pressurized aerosol container. Any propellant or combination of propellants known or otherwise effective for use in such containers, and which are suitable for application to human skin or hair, can be used herein. Suitable propellants include liquifiable gases conventionally used for aerosol containers, most typically volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane, isobutane, and combinations thereof.

Other suitable propellants include hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other suitable propellants include dimethylether, nitrogen, carbon dioxide, nitrous oxide, atmospheric gas, and combinations thereof. Preferred are the hydrocarbon propellants and combinations of hydrocarbon propellants, especially isobutane and combinations containing isobutane.

The aerosol propellant may be mixed with the present hairspray compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the concentration of propellant is from about 10% to about 60%, preferably from about 15% to about 50% , by weight of the total hairspray composition including the propellant.

Other suitable containers or packages include those pressurized aerosol dispensers where the propellant is separated from contact with the hairspray composition. An example of such a package or container would be a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Examples of such dispensers are described in U.S.

Patent 4,077,441, March 7, 1978, Olofsson; U.S. Patent 4,850,577, July 25, 1989, TerStege; and U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, which descriptions are incorporated herein by reference. The hairspray compositions of the present invention may also be dispensed in any known or otherwise effective means for delivery to the hair, including any known or otherwise effective atomizing means such as a nonaerosol pump spray device.

#### Method of Making

The hairspray compositions of the present invention can be made using conventional formulation and mixing techniques. For example, the silicone-containing adhesive block copolymer and the alcohol solvent are combined and mixed together to form a homogeneous solution or dispersion. Other ingredients are then added to the homogenous solution or dispersion and mixed to yield the hairspray composition of the present invention. If the silicone-containing adhesive block copolymer is neutralized, the neutralizer is preferably added prior to addition of other ingredients. The hairspray composition is then packaged in a conventional or otherwise suitable mechanical pump spray device, or alternatively, in the case of aerosol hairspray compositions, the hairspray composition is packaged in a conventional or otherwise suitable aerosol canisters along with an appropriate propellant system.

#### Method of Use

The hairspray compositions of the present invention may be used in a conventional manner to provide the desired hair styling benefits. Such methods generally involve application of an effective amount of the composition to dry hair which has been arranged or positioned in the desired style. In this context, the term "effective amount" means an amount sufficient to provide the hair hold and style benefits desired, typically an amount ranging from about 0.5 grams to about 30 grams of the composition, depending upon the selected hairspray composition and formulation, dispenser type, length of hair, type of hair style, and so forth. The composition is applied to the hair by spraying or atomizing the composition using a mechanical pump spray device, a pressurized aerosol container, or other appropriate delivery means. The composition is then dried or allowed to dry on the applied surface.

The following Experiments and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as

many variations of the invention are possible without departing from its spirit and scope.

### EXAMPLES

The following non-limiting examples illustrate specific embodiments of the hairspray compositions of the present invention, and methods of providing hair styling benefits to dry hair using the compositions. It is understood, however, that various additions or modifications of the specific exemplified embodiments can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the subject invention.

The following exemplified polymers 1.1 and 1.2 are specific silicone-containing adhesive block copolymers suitable for use in the hairspray compositions of the present invention. Each of these exemplified block copolymers are then incorporated into specific hairspray embodiments of the present invention as Examples 2.1, 2.1, 2.3.

#### Polymer 1.1

[Poly(dimethyl siloxane)-block-poly(t-butylacrylate-co-acrylic acid)]<sub>n</sub>.

Place 62.4 parts of t-butyl acrylate, 20.8 parts acrylic acid, 200 parts acetone (as a solvent), and 15 parts isopropanol (as a chain transfer agent) in a roundbottom flask. Separately, dissolve 16.8 parts VPS-1001(poly(dimethyl siloxane)initiator) macroazoinitiator (commercially available from Wako Chemical USA, INC., Richmond, VA) into 200 parts ethyl acetate and add the solution to an addition funnel. Purge the reaction vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction mixture to 58°C. Add the VPS-1001 solution to the reaction flask in a dropwise fashion over the course of one hour. Maintain heating and stirring for 20 hours. Terminate the reaction by opening the reactor to the atmosphere and cooling to room temperature.

The block copolymer is precipitated from the solution by adding one part of the polymer solution to 15 parts water. The resultant polymer is redissolved in acetone and is precipitated again from 15 parts water. The resultant block copolymer is then placed in a vacuum oven for heated drying. Following the drying, the polymer is ground and extracted for 20 hours with hexane using a soxhlet extractor. The polymer is then vacuum dried with heat in an oven. The glass transition

temperature of the block B of the resulting polymer is between about -20°C and 60°C.

Polymer 1.2 [Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)]<sub>n</sub>

Place 80 parts of t-butyl acrylate, 56 parts n-butyl acrylate, 12 parts acrylic acid, 10 parts methacrylic acid, 400 parts acetone (as a solvent), and 50 parts isopropanol (as a chain transfer agent) in a roundbottom flask. Separately, dissolve 20 parts VPS-1001(poly(dimethyl siloxane)initiator) macroazoinitiator (commercially available from Wako Chemical USA, INC., Richmond, VA) into 400 parts ethyl acetate, add to this solution 12 parts acrylic acid and 10 parts methacrylic acid, and add the solution to an addition funnel. Purge the reaction vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction mixture to 58°C. Add the VPS-1001 solution to the reaction flask in a dropwise fashion over the course of one hour. Maintain heating and stirring for 20 hours. Terminate the reaction by opening the reactor to the atmosphere and cooling to room temperature.

The block copolymer is precipitated from the solution by adding one part of the polymer solution to 15 parts water. The resultant polymer is redissolved in acetone and is precipitated again from 15 parts water. The resultant block copolymer is then placed in a vacuum oven for heated drying. Following the drying, the polymer is ground and extracted for 20 hours with hexane using a soxhlet extractor. The polymer is then vacuum dried with heat in an oven. The glass transition temperature of the block B of the resulting polymer is between about -20°C and 60°C.

### Example 2

The following examples represent specific aerosol hairspray embodiments of the present invention.

Component (wt%)	<u>Example Number</u>					
	2.1	2.2	2.3	2.4	2.5	2.6
Copolymer 1.1	5.00	4.00	3.50	---	---	---
Copolymer 1.2	---	---	---	5.00	4.00	3.50
Isododecane <sup>1</sup>	0.50	---	---	0.50	---	---
Triethyl citrate <sup>2</sup>	--	--	0.21	--	--	0.21
Diisobutyl adipate	0.70	0.45	--	0.70	0.45	--

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Propylene glycol	--	--	0.30	--	--	0.30
Sodium hydroxide <sup>3</sup>	1.00	--	--	1.00	--	--
Potassium hydroxide <sup>4</sup>	--	0.94	1.20	--	0.94	1.20
Perfume	0.10	0.10	0.10	0.10	0.10	0.10
Water	QS100	QS100	QS100	QS100	QS100	QS100
Sodium Benzoate	0.10	0.10	--	0.10	0.10	--
Ethanol <sup>5</sup>	56.69	57.42	72.0	56.69	57.42	72.0
Propellant - Isobutane	--	--	7.02	--	--	7.02
Propellant - n-butane	10.00	---	--	10.00	---	--
Propellant - Dimethyl ether <sup>6</sup>	10.00	---	--	10.00	---	--
Propellant - Hydrofluorocarbon 152a <sup>7</sup>	--	25.0	15.98	--	25.0	15.98

<sup>1</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>2</sup> CITROFLEX-2, from Morflex, Inc., Greensboro, NC, USA.

<sup>3</sup> Sodium hydroxide is 30% active.

<sup>4</sup> Potassium hydroxide is 45% active.

<sup>5</sup> SDA 40 (100% ethanol).

<sup>6</sup> DYMEL - A, from Dupont.

<sup>7</sup> DYMEL-152a, from Dupont.

The exemplified hairspray compositions 2.1-2.6 are prepared as described above, by first mixing the silicone-containing adhesive block copolymer (polymer 1.1 or 1.2) with ethanol, neutralizing the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition. Propellants for aerosol embodiments are charged to aerosol containers after the remainder of the prepared composition has been added.

### Example 3

The following examples represent nonaerosol hair spray compositions of the present invention.

Component (wt%)	<u>Example Number.</u>							
	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8
Copolymer 1.1	4.00	5.00	6.00	4.00	---	---	---	---
Copolymer 1.2	---	---	---	---	3.00	3.50	2.50	4.00
Isododecane <sup>1</sup>	1.00	---	---	---	---	1.0	2.0	---
Diisobutyl adipate	0.40	---	0.90	0.55	---	---	---	0.40
Sodium hydroxide <sup>2</sup>	0.96	1.20	1.44	---	---	1.20	---	1.35
Potassium hydroxide <sup>3</sup>	--	--	--	1.21	1.00	--	0.70	--
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0
Sodium Benzoate	--	--	--	--	0.10	0.10	--	0.10
Ethanol <sup>4</sup>	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00

<sup>1</sup> PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

<sup>2</sup> Sodium hydroxide is 30% active.

<sup>3</sup> Potassium hydroxide is 45% active.

<sup>4</sup> SDA 40 (100% ethanol).

The exemplified hairspray compositions 3.1-3.8 are prepared as described above, by first mixing the silicone-containing adhesive block copolymer (polymer 1.1 or 1.2) with ethanol, neutralizing the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition.

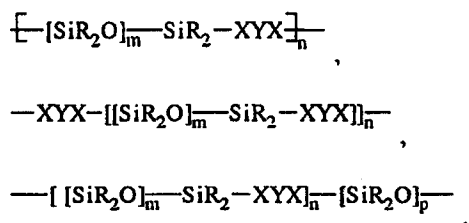
Each of the exemplified hairspray compositions in Examples 2 and 3 are specific embodiment of the hairspray compositions of the present invention, and provide improved hair styling performance when applied to dry, styled or positioned hair, and in particular provide improved maintenance or hold when applied to dry hair and causes minimal or no drooping of the hair during or immediately after application.

Each of the exemplified hair spray compositions in Examples 2 and 3 also provide improved removeability from hair, and when evaluated by the removeability methodology described herein, provide a hair stiffness value of less than 2.0 and a hair flaking value of less than 2.0.

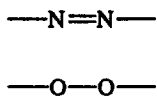
**What is claimed is:**

## 1. A hairspray composition comprising:

- (a) from about 50% to about 99.9% by weight of an alcohol solvent;
- (b) from about 0.1% to about 30% by weight of an adhesive block copolymer having a weight average molecular weight from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with a silicone macroinitiator selected from the group consisting of



and combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof, X is a divalent radical, Y is selected from the group consisting of



and combinations thereof; and m, n, and p are positive integers independently having a value of 1 or greater; and

wherein the silicone macroinitiator has a number average molecular weight from about 500 grams/mole to about 500,000 grams/mole, and the ethylenically unsaturated monomers are copolymerizable and form one or more polymeric blocks within the adhesive block copolymer having a Tg value of from about -20 °C to about 60°C.



2. The hairspray composition of any one of the preceding claims wherein the alcohol solvent is selected from the group consisting of ethanol, n-propanol, isopropanol, and mixtures thereof, and wherein the adhesive block copolymer is solubilized in the hairspray composition.
3. The composition of either of any one of the preceding claims wherein the silicone macroinitiator is a silicone macroazoinitiator where Y is an azo group.
4. The composition of any one of the preceding claims wherein the block copolymers comprise from about 60% to about 95% by weight of the copolymerized ethylenically unsaturated monomers, and from about 5% to about 40% by weight of the copolymerized silicone macroinitiators.
5. The composition of any one of the preceding claims wherein m has a value of from about 14 to about 700, n has a value of from about 1 to about 10, and the silicone macroazoinitiator has a number average molecular weight of from about 5,000 grams/mole to about 100,000 grams/mole.
6. The composition of any one of the preceding claims wherein the composition, when dried, has a cohesive strength of greater than about  $0.5 \text{ kgf/mm}^2$ , a total energy absorption per unit volume of greater than about  $0.55 \text{ kgfmm/mm}^3$  and an impact strength of greater than about 7000 ergs.
7. The composition of any one of the preceding claims wherein the composition, when dried, has a cohesive strength of greater than about  $0.7 \text{ kgf/mm}^2$ , a total energy absorption of greater than about  $1.10 \text{ kgfmm/mm}^3$ , and an impact strength of greater than about 50,000 ergs.

8. The composition of any one of the preceding claims wherein the vinyl monomer units are selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, butadiene, cyclohexadiene, ethylene, propylene n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.

9. A composition according to any one of preceding claims wherein the composition provides a hair stiffness value of from 0 to about 2.5 and a hair flaking value of from 0 to about 2.5

10. A method of styling hair comprising the step of applying to dry, positioned hair an effective amount of the composition of any one of the preceding claims.

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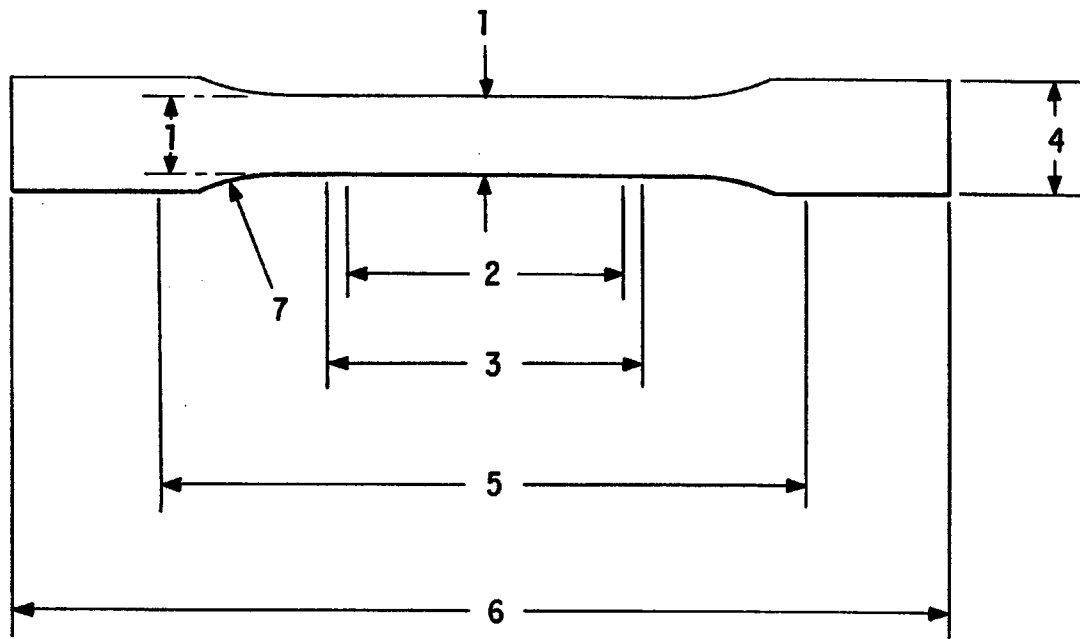


FIG. 1

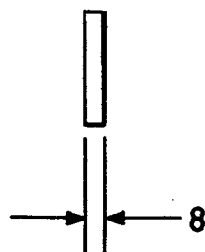


FIG. 2

# INTERNATIONAL SEARCH REPORT

national Application No

PCT/IB 98/00784

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/06 C08G77/442 C09D183/10 C08L83/10 C08F293/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08G C09D C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 766 957 A (WAKO PURE CHEMICAL IND.) 9 April 1997 cited in the application see column 7, line 52-56; claims 1-7 ----	1-10
A	EP 0 659 838 A (WACKER CHEMIE) 28 June 1995 see claims 1,2 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

27 August 1998

Date of mailing of the international search report

04/09/1998

Name and mailing address of the ISA

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Beyss, E

# INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 766957 A	09-04-1997	CN 1158720 A JP 9157339 A	10-09-1997 17-06-1997
EP 659838 A	28-06-1995	DE 4338421 A AT 136322 T CA 2118173 A DE 59400185 D ES 2085817 T JP 2693391 B JP 7188414 A US 5523365 A	11-05-1995 15-04-1996 11-05-1995 09-05-1996 01-06-1996 24-12-1997 25-07-1995 04-06-1996



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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C08F 290/04, A61K 7/08</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/01383</b> <b>(43) International Publication Date:</b> 12 January 1995 (12.01.95)
<b>(21) International Application Number:</b> PCT/US94/07385 <b>(22) International Filing Date:</b> 30 June 1994 (30.06.94)  <b>(30) Priority Data:</b> 08/086,605 1 July 1993 (01.07.93) US 08/257,962 16 June 1994 (16.06.94) US 08/259,070 20 June 1994 (20.06.94) US  <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors:</b> TORGERSON, Peter, Marte; 4127 U.S. Route 35 N.W., Washington Crt House, OH 43160 (US). MIDHA, Sanjeev; 9247 Deercross Parkway, Blue Ash, OH 45236 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> THERMOPLASTIC ELASTOMERIC COPOLYMERS AND HAIR AND SKIN CARE, COMPOSITIONS CONTAINING THE SAME  <b>(57) Abstract</b>  The present invention relates to water or alcohol soluble or dispersible thermoplastic elastomeric copolymers and to cosmetic and pharmaceutical compositions containing these copolymers. This invention especially relates to copolymers useful for hair styling purposes, and the hair styling compositions containing these copolymers. This invention further relates to copolymers useful for providing cosmetic and pharmaceutical compositions for topical application to the skin. These topical skin care compositions are useful for delivering and/or transdermally transporting active ingredients to or through the skin.		

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THERMOPLASTIC ELASTOMERIC COPOLYMERS AND HAIR AND  
SKIN CARE  
COMPOSITIONS CONTAINING THE SAME

5

TECHNICAL FIELD

The present invention relates to water or alcohol soluble or dispersible thermoplastic elastomeric copolymers and to cosmetic and pharmaceutical compositions containing these copolymers. These copolymers are useful for hair setting and styling purposes. A particularly useful application for these copolymers is in hair spray and mousse compositions. This invention further relates to copolymers useful for incorporating into cosmetic and pharmaceutical compositions for topical application to the skin. Skin care compositions containing these copolymers are useful for delivering and/or transdermally transporting a wide variety of active ingredients to and/or through the skin.

BACKGROUND OF THE INVENTION

In the hair care area, the desire to have hair retain a particular style or shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration of the hair fiber or temporary alteration of hair style or shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. Products in the form of mousses, gels, lotions, or sprays are most commonly used for this purpose. Once the desired style is achieved, spray products are commonly used to help retain the style. These various hair care products utilize a variety of gums and resins for providing styling and retention. However, the gums and resins currently used tend to feel either too sticky or too stiff upon the hair. Also, these gums and resins do not wash out as easily as desired. Therefore, the need exists for improved styling and style retention materials which provide a strong, lasting, hold without being either too stiff or too sticky, and yet which are easily removed by shampooing.

Furthermore, because most hair care styling compositions are water and/or alcohol based, it is necessary that these materials have good solubility or dispersibility in these bases.

Thermoplastic elastomeric copolymers are well known. These  
5 copolymers combine thermoplastic properties, which give them solubility and strength, with rubber-like elastic properties, which give them flexibility and shape retention. However, despite these highly desirable properties, most thermoplastic elastomeric copolymers are generally insoluble or  
10 poorly soluble in water and/or alcohol systems and would not be suitable in hair care compositions. Therefore, thermoplastic elastomeric copolymers having good water and/or alcohol solubility would be useful for developing improved hair care compositions.

In the present invention new classes of thermoplastic elastomeric copolymers have been developed which have the desired flexibility,  
15 strength, and elastic properties and yet are readily soluble and/or dispersible in water and/or alcohol systems. Furthermore, these materials provide hair care compositions which leave the hair feeling natural, i.e. not stiff.

In addition to the hair care benefits provided by these copolymers, it  
20 has been found that these materials are also useful for incorporation into a wide variety of cosmetic and pharmaceutical compositions for topical application to the skin. These copolymers provide topical compositions which are more easily and uniformly spread upon the skin, which feel good upon the skin, and yet which are highly substantive. Furthermore,  
25 these copolymers are useful for enhancing the penetration of a wide variety of cosmetic and pharmaceutical actives into the skin, or alternatively, through the skin for systemic delivery.

It is an object of the present invention to provide novel, water and/or alcohol soluble and/or dispersible thermoplastic elastomeric copolymers.

30 It is another object of the present invention to provide novel thermoplastic elastomeric copolymers useful in hair care compositions.

It is another object of the present invention to provide novel hair care compositions having improved styling and/or hold properties and having improved aesthetics.

35 It is another object of the present invention to provide novel

thermoplastic elastomeric copolymers useful in topical skin care cosmetic and pharmaceutical compositions.

It is another object of the present invention to provide novel topical cosmetic and pharmaceutical compositions useful for delivering a wide  
 5 variety of cosmetic materials and pharmaceutical actives to and/or through the skin.

These and other objects will become readily apparent from the detailed description which follows.

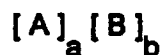
### SUMMARY OF THE INVENTION

10 The present invention relates to a water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and two or more polymeric pendant side chains, said copolymer formed from the copolymerization of randomly repeating A and B units wherein said copolymer comprises:

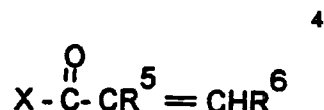
- 15 (i) from about 40% to about 90% by weight of said A units, wherein said A units are polymerizable monomer units; and
- (ii) from about 10% to about 60% by weight of said B units, wherein said B units are hydrophilic macromonomer units copolymerizable with A, whereby said macromonomer units  
 20 form said pendant polymeric side chains;

wherein said copolymer has a weight average molecular weight greater than about 10,000, and wherein said copolymer exhibits two distinct  $T_g$  values, said first  $T_g$  corresponding to said backbone and having a value less than about  $0^\circ\text{C}$ , and said second  $T_g$  corresponding to said side  
 25 chains and having a value greater than about  $25^\circ\text{C}$ .

The present invention also relates to a water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and two or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units and corresponding  
 30 to the formula

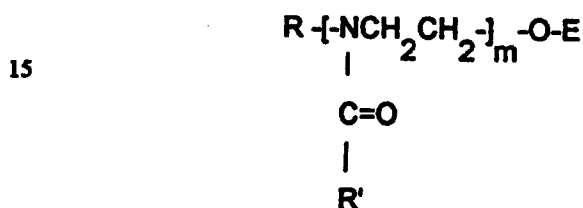


wherein A is at least one polymerizable monomer unit corresponding to the formula



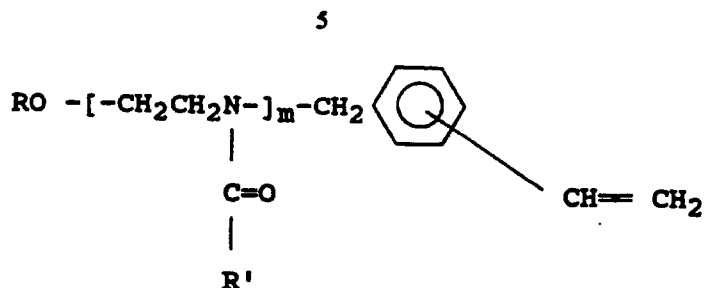
wherein X is selected from the group consisting of -OH, -OM, -OR<sup>4</sup>, -NH<sub>4</sub><sup>+</sup>, -NHR<sup>4</sup>, and -N(R<sup>4</sup>)<sub>2</sub>; M is a cation selected from the group consisting of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Zn<sup>++</sup>, NH<sub>4</sub><sup>+</sup>, alkylammonium, dialkylammonium, trialkylammonium, and tetralkylammonium; each R<sup>4</sup> is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R<sup>5</sup> and R<sup>6</sup> are independently selected from the group consisting of H, C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl, and 2-ethoxyethyl.

B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



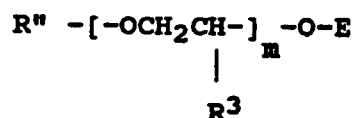
wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, and 4-vinylbenzoyl; R and R' are independently selected from the group consisting of H and C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl; m is an integer from about 10 to about 2000; a is an integer of about 100 or greater; and b is an integer of about 2 or greater.

In further embodiments, B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



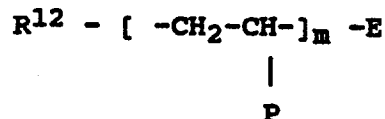
wherein R and R' are independently selected from the group consisting of H and C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl; m is an integer from about 10 to about 2000; a is an integer of about 100 or greater; and b is an integer of about 2 or greater.

In further embodiments, B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzoyl, and 4-vinylbenzoyl, and mixtures thereof; R'' is selected from the group consisting of C<sub>1</sub>-C<sub>40</sub> straight or branched chain alkyl; R<sup>3</sup> is selected from the group consisting of H, and C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl; m is an integer from about 20 to about 2000; a is an integer of about 100 or greater; and b is an integer of about 2 or greater.

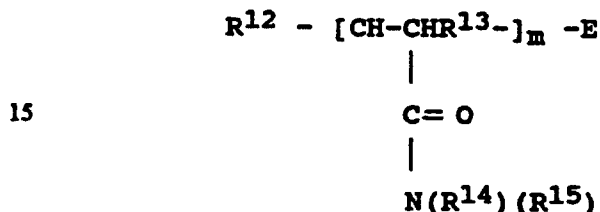
In further embodiments, B is at least one hydrophilic macromonomer unit copolymerizable with A corresponding to the formula



wherein E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 2-vinyl benzyl, 3-vinyl benzyl, 4-vinyl benzyl, and mixtures thereof; R<sup>12</sup> is selected from the group consisting of hydrogen, C1-6

straight or branched chain alkyl, benzyl, 1-phenyl substituted C2-6  
 straight or branched chain alkyl, 1,1-diphenyl substituted C2-6 straight or  
 branched chain alkyl, and mixtures thereof; P is a polar moiety selected  
 from the group consisting of 2-pyridyl, 3-pyridyl, 4-pyridyl, halogen  
 5 substituted 2-, 3-, or 4-pyridyl, C1-4 alkyl substituted 2-, 3-, or 4-pyridyl, 2-  
 aminophenyl, 3-aminophenyl, 4-aminophenyl, 2-aminomethylphenyl, 3-  
 aminomethylphenyl, 4-aminomethylphenyl, 2-aminoethylphenyl, 3-  
 aminoethylphenyl, and 4-aminoethylphenyl, and pharmaceutically  
 acceptable salts and quaternized derivatives thereof, and mixtures  
 10 thereof; and m is an integer from about 20 to about 2000.

In further embodiments, B is at least one hydrophilic macromonomer  
 unit copolymerizable with A and C corresponding to the formula



wherein E is an ethylenically unsaturated moiety, copolymerizable with A,  
 selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl,  
 20 ethacryloyl, 2-vinyl benzyl, 3-vinyl benzyl, 4-vinyl benzyl, and mixtures  
 thereof;  $R^{12}$  is selected from the group consisting of hydrogen, C1-C6  
 straight or branched chain alkyl, benzyl, 1-phenyl substituted C2-6  
 straight or branched chain alkyl, 1,1-diphenyl substituted C2-6 straight or  
 branched chain alkyl, and mixtures thereof; and  $R^{13}$  is selected from the  
 25 group consisting of H and C1-6 straight or branched chain alkyl, and  $R^{14}$ ,  
 and  $R^{15}$  are independently selected from the group consisting of C1-8  
 straight or branched chain alkyl; and m is an integer from about 20 to  
 about 2000.

In further embodiments, the present invention relates to hair care  
 30 compositions, especially hair setting and styling compositions, containing  
 these copolymers.

In further embodiments, the present invention relates to cosmetic and  
 pharmaceutical compositions containing these copolymers for topical  
 application to the skin for the delivery of cosmetic materials and  
 35 pharmaceutical actives onto, into and/or through the skin.

All percentages and ratios used herein are by weight of the total composition and all measurements made are at 25°C, unless otherwise designated. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as optional ingredients and components described herein.

#### DETAILED DESCRIPTION OF THE INVENTION

The term "thermoplastic elastomeric copolymer" as used herein means that the copolymer has both thermoplastic and elastomeric properties. The term "thermoplastic elastomeric copolymer" is one familiar to those of ordinary skill in polymer science. By "thermoplastic" is meant that upon heating, the copolymer softens and upon cooling it rehardens; upon being subject to stress it begins to flow and upon removal of stress it stops flowing. By "elastomeric" is meant that the copolymer has an elastic modulus such that the copolymer exhibits a resistance to deformation and has limited extensibility and retraction. In other words, the copolymer tends to recover its size and shape after deformation.

The term "macromonomer" is one familiar to those of ordinary skill in polymer science, and is used to describe a polymeric material containing a polymerizable moiety. A macromonomer is a macromolecular monomer. A macromonomer is essentially a very large type of monomer building block unit which can be used in a polymerization reaction to form polymers with itself, with other monomers, or with other macromonomers.

The term "water or alcohol soluble or dispersible" as used herein means that these copolymers are either freely soluble in or dispersible (as a stable suspension) in at least one of the following solvents, or alternatively, in any combination of one of the following solvents: water, methanol, ethanol, and isopropanol. By "soluble" is meant that the copolymer is soluble in the solvent or solvents at 25°C at a concentration of at least about 20 mg/mL, more preferably about 50 mg/mL, and most preferably about 100 mg/mL. By "dispersible" is meant that the copolymer forms a stable, uniform suspension (without the addition of further materials such as emulsifiers) when combined with the solvent or solvents at 25°C at a concentration of at least about 20 mg/mL, more preferably about 50 mg/mL, and most preferably about 100 mg/mL.

#### Thermoplastic Elastomeric Copolymers

The copolymers of the present invention are characterized in having an elastomeric or flexible backbone and rigid, thermoplastic, hydrophilic side chains. This combination of both elastomeric and thermoplastic moieties in a single copolymer provides the unique and useful properties of these materials. The copolymers of the present invention, can also be referred to as "graft copolymers" because they can be prepared from the copolymerization of monomer units and macromonomer units. In other words, the macromonomer is "grafted" or incorporated into the copolymer.

These copolymers exhibit two distinct immiscible phases. Without being limited by theory, it is believed that the hydrophilic side chains of these copolymers are closely associated with each other, thereby existing in one phase, while the backbone of the copolymer remains in a separate phase. A consequence of this phase immiscibility is that these copolymers exhibit two distinct glass transition temperatures or, " $T_g$ 's", for the backbone and the side chains.  $T_g$  is a well known term of art in polymer science used to describe the temperature at which a polymer or portion thereof undergoes a transition from a solid or brittle material to a liquid or rubber-like material. Glass transition temperatures can be measured using standard techniques that are well known to the polymer scientist of ordinary skill in the art. One particularly useful technique for determining glass transitions is differential scanning calorimetry (also known as DSC). The glass transition phenomenon in polymers is described in Introduction to Polymer Science and Technology: An SPE Textbook, (eds. H.S. Kaufman and J.J. Falcetta), (John Wiley & Sons: 1977), which is incorporated by reference herein in its entirety.

The  $T_g$  of the backbone of the copolymers herein (i.e. that part of the copolymer not containing the side chains) should be less than about  $0^{\circ}\text{C}$ . Preferably the  $T_g$  of the backbone should be from about  $-10^{\circ}\text{C}$  to about  $-130^{\circ}\text{C}$ , more preferably from about  $-20^{\circ}\text{C}$  to about  $-125^{\circ}\text{C}$ , and most preferably from about  $-55^{\circ}\text{C}$  to about  $-120^{\circ}\text{C}$ . The  $T_g$  of the side chain of the copolymers (i.e. that part of the copolymer not containing the backbone) is greater than about  $20^{\circ}\text{C}$ . Preferably the  $T_g$  of the sidechain should be from about  $25^{\circ}\text{C}$  to about  $200^{\circ}\text{C}$ , more preferably from about  $30^{\circ}\text{C}$  to about  $175^{\circ}\text{C}$ , and most preferably from about  $35^{\circ}\text{C}$  to about  $150^{\circ}\text{C}$ .



Because these copolymers possess two distinct  $T_g$ 's, these copolymers are useful in hair styling and setting compositions. Without being limited by theory, it is believed that when these copolymers are subjected to temperatures above both  $T_g$ 's, they are essentially liquid and can provide great flexibility during the styling process (e.g., when curling irons, blow driers, and other heat sources are applied to the hair). Upon cooling of the copolymer to room temperature (e.g., when the heat source is removed from the hair) the copolymer is then at a temperature that is typically between both  $T_g$ 's, and the copolymer possesses structural rigidity from the macromonomer side chains, and yet has flexibility from the backbones, and can provide a strong, yet flexible, hair hold or style retention.

Furthermore, at skin temperatures, these copolymers would be at a temperature which is essentially between both  $T_g$ 's. These copolymers can enhance the film forming properties of skin care compositions, and provide benefits such as better and more even distribution upon the skin.

The copolymers of the present invention are formed from the copolymerization of randomly repeating A and B units, preferably wherein the A units are selected from at least one polymerizable, ethylenically unsaturated monomer unit, and the B units are selected from at least one hydrophilic macromonomer unit which contains an ethylenically unsaturated moiety which is copolymerizable with A. In typical embodiments of these copolymers, the backbone is primarily derived from the ethylenically unsaturated portion of the A monomer unit and the ethylenically unsaturated portion of the B macromonomer unit. The side chains are derived from the non-copolymerized portions of the macromonomer. The A and B units can be selected from a wide variety of structures as long as the limitations of the copolymer are met (e.g., solubility,  $T_g$ 's, and molecular weights).

The A monomer units of the copolymers of the present invention can comprise from about 40% to about 90%, more preferably from about 50% to about 85%, and most preferably from about 60% to about 80%, by weight, of the copolymers.

The hydrophilic B macromonomer units can comprise from about 10%

to about 60%, more preferably from about 15% to about 50%, and most preferably from about 20% to about 40%, by weight of the copolymers.

The copolymers of the present invention have a weight average molecular weight of at least about 10,000. There is no upper limit for  
5 molecular weight except that which limits applicability of the invention for practical reasons, such as viscosity, processing, aesthetic characteristics, formulation compatibility, etc. In general, the weight average molecular weight is less than about 5,000,000, more generally less than about 2,500,000, and typically less than about 1,500,000. Preferably, the  
10 weight average molecular weight is from about 10,000 to about 5,000,000, more preferably from about 75,000 to about 1,000,000, even more preferably from about 100,000 to about 850,000, and most preferably from about 125,000 to about 750,000.

Alternatively, the copolymers of the present invention can also be  
15 represented by the formula



wherein A and B are as described herein, and where a is an integer of about 100 or greater, preferably a is an integer from about 100 to about 3000, more preferably from about 250 to about 2000, and most preferably  
20 from about 350 to about 1500, and b is an integer of about 2 or greater, preferably from about 2 to about 50, more preferably from about 2 to about 20, and most preferably from about 2 to about 10. In this formula, it is expressly intended that even though ranges are provided for the subscripts a and b, these subscripts are not intended to strictly limit the  
25 polymers herein so long as the physical propoerties of the polymers are achieved. When the copolymers herein are described by the formula disclosed in this paragraph it has been found useful to describe the copolymers by their number average molecule weights. In general, the number average molecular weight is less than about 2,500,000, more  
30 generally less than about 1,500,000, and typically less than about 1,000,000. Preferably, the number average molecular weight is from about 15,000 to about 1,000,000, more preferably from about 20,000 to about 500,000, and most preferably from about 25,000 to about 250,000.

By appropriate selection and combination of the particular A and B  
35 units and by the choice of specific relative ratios of the units well within

the ability of one of ordinary skill in the art, the copolymers can be optimized for various physical properties such as solubility,  $T_g$ 's, and the like, and for compatibility with other ingredients commonly used in hair care and skin care applications.

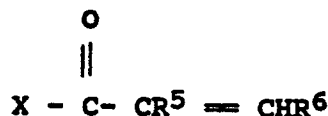
- 5 When the copolymers of the present invention are incorporated into hair and/or skin care compositions, the copolymers typically comprise from about 0.1% to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 10%, and most preferably from about 2% to about 5% of the composition, although higher or lower  
10 amounts can be used depending upon the particular application.

#### Monomer "A" Units

- The "A" monomer unit is selected from polymerizable monomers, preferably ethylenically unsaturated monomers. Either a single A monomer or combinations of two or more A monomers can be utilized.  
15 For example, if two different A monomers are polymerized with a B macromonomer, the resulting copolymer could be described as a terpolymer. In either case, the monomers are selected to meet the requirements of the copolymer. By "polymerizable", as used herein, is meant monomers that can be polymerized using any conventional  
20 synthetic techniques. Monomers that are polymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean monomers that contain at least one polymerizable carbon-carbon double bond (which can be mono-, di-, tri-, or tetra-substituted).

- 25 The A monomer units of the copolymers of the present invention can comprise from about 40% to about 90%, more preferably from about 50% to about 85%, and most preferably from about 60% to about 80%, by weight, of the copolymers.

- 30 The ethylenically unsaturated A monomer units preferably can be described by the following formula



- wherein X is selected from the group consisting of -OH, -OM, -OR<sup>4</sup>, -NH<sub>2</sub>,  
35 -NHR<sup>4</sup>, and -N(R<sup>4</sup>)<sub>2</sub>; M is a cation selected from the group consisting of

Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Zn<sup>++</sup>, NH<sub>4</sub><sup>+</sup>, alkylammonium, dialkylammonium, trialkylammonium, and tetralkylammonium; each R<sup>4</sup> is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R<sup>5</sup> and R<sup>6</sup> are independently selected from the group consisting of H, C<sub>1</sub>-C<sub>8</sub> straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl, and 2-ethoxyethyl.

Representative nonlimiting examples of monomers useful herein include acrylic acid and salts, esters, and amides thereof. The salts can be derived from any of the common nontoxic metal, ammonium, or substituted ammonium counter ions. The esters can be derived from C<sub>1</sub>-C<sub>40</sub> straight chain, C<sub>3</sub>-C<sub>40</sub> branched chain, or C<sub>3</sub>-C<sub>40</sub> carbocyclic alcohols; from polyhydric alcohols having from about 2 to about 8 carbon atoms and from about 2 to about 8 hydroxy groups (nonlimiting examples of which include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, glycerin, and 1,2,6-hexanetriol); from amino alcohols (nonlimiting examples of which include aminoethanol, dimethylaminoethanol, and diethylaminoethanol, and their quaternized derivatives); or from alcohol ethers (nonlimiting examples of which include methoxyethanol, and ethoxy ethanol). The amides can be unsubstituted, N-alkyl or N-alkylamino mono-substituted, or N,N-dialkyl or N,N-dialkylamino di-substituted, wherein the alkyl or alkylamino group can be derived from C<sub>1</sub>-C<sub>40</sub> straight chain, C<sub>3</sub>-C<sub>40</sub> branched chain, or C<sub>3</sub>-C<sub>40</sub> carbocyclic moieties. Additionally, the alkylamino groups can be quaternized. Also useful as monomers are substituted acrylic acids and salts, esters, and amides thereof (wherein the substituents are on the two and three carbon positions of the acrylic acid and are independently selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, -CN, -COOH (e.g., methacrylic acid, ethacrylic acid, and 3-cyano acrylic acid). The salts, esters, and amides of these substituted acrylic acids can be defined as described above for the acrylic acid salts, esters, and amides. Other useful monomers include vinyl and allyl esters of C<sub>1</sub>-C<sub>40</sub> straight chain, C<sub>3</sub>-C<sub>40</sub> branched chain, or C<sub>3</sub>-C<sub>40</sub> carbocyclic carboxylic acids; vinyl and allyl halides (e.g., vinyl chloride and allyl chloride); vinyl and allyl substituted heterocyclic compounds (e.g., vinyl pyridine and allyl pyridine); vinylidene chloride;

and hydrocarbons having at least one carbon-carbon double bond (e.g., styrene, alpha-methylstyrene, t-butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, vinyl toluene); and mixtures thereof.

- 5 Preferred A monomers useful herein include those selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, methyl ethacrylate, ethyl ethacrylate, n-butyl ethacrylate, iso-butyl ethacrylate, t-butyl ethacrylate, 2-ethylhexyl ethacrylate, decyl ethacrylate, 2,3-dihydroxypropyl acrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxypropyl methacrylate, glyceryl monoacrylate, glyceryl monomethacrylate, acrylamide, methacrylamide, ethacrylamide, N-methyl acrylamide, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N-ethylacrylamide, N-isopropyl acrylamide, N-butyl acrylamide, N-t-butyl acrylamide, N,N-di-n-butylacrylamide, N,N-diethylacrylamide, N-octyl acrylamide, N-octadecyl acrylamide, N-phenyl acrylamide, N-methyl methacrylamide, N-ethylmethacrylamide, N-dodecylmethacrylamide, N,N-dimethylaminoethyl acrylamide, quaternized N,N-dimethylaminoethyl acrylamide, N,N-dimethylaminoethyl methacrylamide, quaternized N,N-dimethylaminoethyl methacrylamide, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, quaternized N,N-dimethylaminoethyl acrylate, quaternized N,N-dimethylaminoethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate, glyceryl acrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-methoxyethyl ethacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-ethoxyethyl ethacrylate, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, angelic acid, diallyldimethyl ammonium chloride, vinyl pyrrolidone, methyl vinyl ether, methyl vinyl ketone, maleimide, vinyl pyridine, vinyl imidazole, vinyl furan, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof. More preferred A monomers are those selected from
- 10  
15  
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the group consisting of methyl acrylate, methyl methacrylate, methyl ethacrylate, ethyl acrylate, ethyl methacrylate, ethyl ethacrylate, n-butyl acrylate, n-butyl methacrylate, n-butyl ethacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-ethylhexyl ethacrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, and mixtures thereof.

Most preferred A monomers are those selected from the group consisting of n-butyl acrylate, 2-ethylhexyl acrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, and mixtures thereof.

#### Hydrophilic "B" Macromonomer Units

A macromonomer is a large monomer unit, i.e. a macromolecular monomer, which can be further polymerized with itself, with other conventional monomers, or with other macromonomers. The term "macromonomer" is one that is familiar to the polymer chemist of ordinary skill in the art. The hydrophilic "B" macromonomer units of the present invention are very large monomer building blocks which can be formed from the polymerization of smaller monomer units. The B macromonomers encompass a wide variety of structures and are copolymerizable with the A monomer. Either a single B macromonomer or combinations of two or more B macromonomers can be utilized. In either case, the macromonomers are selected to meet the requirements of the copolymer.

The hydrophilic B macromonomers comprise from about 10% to about 60%, more preferably from about 15% to about 50%, and most preferably from about 20% to about 40%, by weight of the copolymers.

By the term "copolymerizable" as used herein is meant B macromonomers that can be reacted with the A monomer in a polymerization reaction using any conventional synthetic techniques. "Copolymerization" is a term of art used to refer to the simultaneous polymerization of two or more different monomers. In the present invention, B macromonomers that are copolymerizable with A monomers using conventional free radical initiated techniques are preferred. By the term "hydrophilic" as used herein is meant B macromonomers that are soluble in or have an affinity for water and/or other polar, water-soluble

solvent materials (e.g., methanol, ethanol, propanol, isopropanol and the like). "Hydrophilic" is also a term of art used to describe a substance having a strong tendency to absorb water which results in the swelling, solubilization, or dispersion of the substance in water. Without being  
5 limited by theory, the hydrophilic B macromonomer units are believed to contribute to the overall water or alcohol soluble or dispersible properties of the copolymers.

B macromonomers that are useful herein contain an ethylenically unsaturated moiety that is copolymerizable with the A monomer. The  
10 term "ethylenically unsaturated" is used herein to mean B macromonomers that contain at least one carbon-carbon double bond (which can be mono-, di-, tri-, or tetra-substituted). Typically, the preferred B macromonomers are those that are endcapped with the ethylenically unsaturated moiety. By "endcapped" as used herein is  
15 meant that the ethylenically unsaturated moiety is at or near a terminal position of the macromonomer. However, this definition of "endcapped" is not intended to limit the macromonomer to only those macromonomers which terminate in a carbon-carbon double bond (whether mono-, di-, tri-, or tetra-substituted).

20 The hydrophilic B macromonomers of the present invention can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically the weight average molecular weight of the  
25 macromonomer is from about 1000 to about 200,000, more preferably from 1500 to about 30,000, and most preferably from about 2000 to about 25,000.

For example, the hydrophilic B macromonomers can be synthesized by the polymerization (acid, base, free radical, or auto-initiated) of a  
30 hydrophilic monomer to form a polymer which is subsequently reacted with or "endcapped" with a structural unit E, containing the ethylenically unsaturated moiety. Alternatively, the B macromonomers can be synthesized starting with commercially available hydrophilic polymers which are "endcapped" with the structural unit E. In yet another  
35 alternative, the B macromonomer can be synthesized by starting with the

structural unit E, and polymerizing onto it the desired hydrophilic monomer units. It is to be understood that in this third alternative, the ethylenically unsaturated moiety of the E unit is not consumed in the synthesis but its integrity is preserved for subsequent copolymerization of the B macromonomer with the A monomer units. All of the synthetic alternatives are merely illustrative in that any other suitable synthetic procedures can be utilized to prepare the B macromonomers and copolymers of the present invention.

The B macromonomers can be described by the following formula



X is a hydrophilic monomer unit, and m is an integer from about 10 to about 2000, preferably from about 15 to about 300, and more preferably from about 20 to about 250, so that the macromonomer meets the weight average molecular weight requirements set forth above. Preferred is when X is a hydrophilic monomer unit selected from the group consisting of oxazolines, N-alkyloxazolines, alkylene glycols, N-vinylpyrrolidones, N-allylpyrrolidones, vinylpyridines, allylpyridines, vinylcaprolactams, allylcaprolactams, vinylimidazoles, allylimidazoles, vinylfurans, allylfurans, vinyltetrahydrofurans, allyltetrahydrofurans, vinylaminobenzenes, vinylaminomethylbenzenes, vinylaminoethylbenzenes, N,N-dialkylacrylamides, N,N-dialkyl(alkyl)acrylamides, and mixtures thereof. More preferred is wherein X is a monomer unit selected from the group consisting of N-alkyloxazolines, alkylene glycols, vinylpyridines, N,N-dialkylacrylamides, N,N-dialkyl(alkyl)acrylamides, and mixtures thereof. Most preferred is wherein X is a monomer unit selected from vinylpyridines.

E is a structural unit containing the ethylenically unsaturated moiety or "endcapping" group. Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, isoprenyl, cyclohexyl, cyclopentyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected



from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof.

I is an optionally present chemical moiety. In other words, n is an integer selected from zero and one. Without being limited by theory, I can be derived from a chemical initiator or solvent used in the synthesis of the B macromonomer. Nonlimiting examples of such initiators from which I can be derived include hydrogen ion, hydrogen radical, hydride ion, hydroxide ion, hydroxyl radical, peroxide radical, peroxide anion, C1-20 carbocations, C1-20 carbanions, C1-20 carbon radicals, C1-20 aliphatic and aromatic alkoxy anions, ammonium ion, and substituted ammonium ions (e.g., C1-20 alkyl and C1-20 alkoxy substituted). I can be derived from any useful solvent, nonlimiting examples of which include water, methanol, ethanol, propanol, isopropanol, acetone, hexane, dichloromethane, chloroform, benzene, and toluene. Nonlimiting examples of I include chemical moieties selected from the group consisting of H, C1-C6 alkyl, phenyl, 4-methylphenyl, and benzyl; preferably H, methyl, ethyl, and phenyl; and more preferably H, methyl, and ethyl.

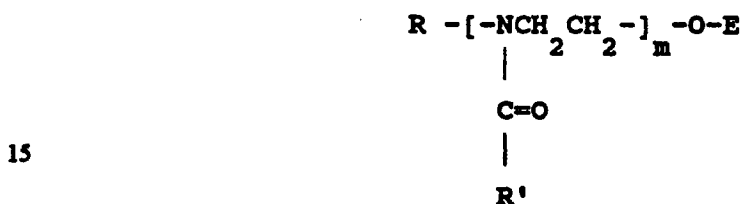
Representative examples of classes of endcapped B macromonomers useful herein include those selected from the group consisting of endcapped poly(N-alkyloxazolines), endcapped polyalkylene glycols, endcapped polyalkylene glycol monoalkyl ethers, endcapped poly(N-vinylpyrrolidones), endcapped poly(N-allylpyrrolidones), endcapped polyvinylpyridines, endcapped polyallylpyridines, endcapped polyvinylcaprolactams, endcapped polyallylcaprolactams, endcapped polyvinylimidazoles, endcapped polyallylimidazoles, endcapped polyvinylfurans, endcapped polyvinyltetrahydrofurans, endcapped polyallylfurans, endcapped polyacrylic acids, endcapped polymethacrylic acids, endcapped polyallyltetrahydrofurans, endcapped polyvinylaminobenzenes, endcapped polyvinyl (N,N-dialkylaminobenzenes), endcapped polyvinyl (N-alkylaminobenzenes), endcapped polyvinylaminomethylbenzenes, endcapped polyvinyl (N,N-dialkylaminomethylbenzenes), endcapped polyvinyl (N-alkylaminomethylbenzenes), endcapped polyvinylaminoethylbenzenes, endcapped polyvinyl (N,N-dialkylaminoethylbenzenes), endcapped

polyvinyl (N-alkylaminoethylbenenes), endcapped poly(N,N-dialkylacrylamides), endcapped poly(N,N-dialkyl(alkyl)acrylamides), and mixtures thereof.

Preferred are macromonomers selected from the group consisting of endcapped poly(N-alkyloxazolines), endcapped polyalkylene glycols, endcapped polyalkylene glycol monoalkyl ethers, endcapped polyvinylpyridines, endcapped polyacrylamides, and mixtures thereof.

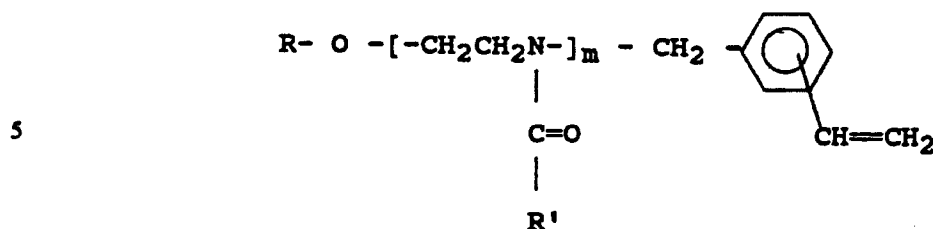
More preferred are endcapped polyvinylpyridine and endcapped polyacrylamide macromonomers.

Examples of endcapped poly(N-alkyloxazoline) macromonomers are those having the following chemical formula:



wherein R and R' are independently selected from H or C<sub>1-8</sub> straight or branched chain alkyl, more preferably R and R' are independently selected from H, methyl, or ethyl; and most preferably R is methyl and R' is ethyl. E is a copolymerizable, ethylenically unsaturated moiety (i.e. the endcapping moiety). Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, isoprenyl, cyclohexyl, cyclopentyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof. In the above structure m is preferably an integer from about 10 to about 2000, more preferably from about 15 to about 300, and most preferably from about 20 to about 250. Alternatively, other examples of endcapped poly(N-alkyloxazoline) macromonomers are those having the following chemical

formula:



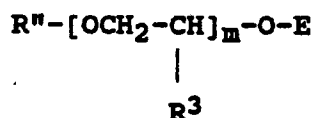
wherein R and R' are independently selected from the group consisting of H or C<sub>1-8</sub> straight or branched chain alkyl, more preferably R and R' are independently selected from H, methyl, or ethyl; and most preferably R is H and R' is ethyl. In the above structure m is an integer from about 10 to about 2000, more preferably from about 15 to about 300, and most preferably from about 20 to about 250. Highly preferred examples of endcapped poly(N-alkyloxazoline) macromonomers useful herein include acryloyl endcapped poly(2-ethyl oxazoline), methacryloyl endcapped poly(2-ethyl oxazoline), styryl endcapped poly(2-ethyloxazoline), acryloyl endcapped poly(2-methyl oxazoline), methacryloyl endcapped poly(2-methyl oxazoline), 3-vinylbenzoyl endcapped poly(2-methyloxazoline), 4-vinylbenzoyl endcapped poly(2-methyloxazoline), and mixtures thereof.

The endcapped poly(N-alkyloxazoline) macromonomers can be synthesized using standard synthetic procedures which involve polymerizing, usually under acid-catalyzed conditions, an N-alkyloxazoline to yield a poly(N-alkyloxazoline) alcohol. This alcohol can then be subsequently endcapped, employing standard reaction procedures, with the desired ethylenically unsaturated moiety using a reactive or activated form of an endcapping group. Suitable activated endcapping groups include vinyl, allyl, 1-propenyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, and 4-vinylbenzoyl halides (e.g. chlorides, bromides, and iodides), and the acid chlorides and bromides derived from acrylic acid, methacrylic acid, and ethacrylic acid. See, e.g., S.I. Shoda et al., "Synthesis and Surfactant Property of Copolymers Having a Poly(2-Oxazoline) Graft Chain", *Journal of Polymer Science: Part A: Polymer Chemistry*, vol. 30, pp. 1489-1494 (1992); T. Saegusa et al., "Macromolecular Engineering on the Basis of the Polymerization of 2-Oxazolines, *Makromol. Chem., Macromol. Symp.*, vol. 51, pp. 1-10 (1991);

S. Kobayashi et al., Macromolecules, vol 22, pp. 2878-2884 (1989), and U.S. Patent No. 4,011,376, to Tomalia et al., issued March 8, 1977; and U.S. Patent No. 3,786,116, to Milkovich et al., issued January 15, 1974; all of which are incorporated herein by reference.

Alternatively the polyoxazoline macromonomers can be synthesized by polymerizing the monomers onto an appropriate endcapping group. For example, the vinyl benzyl endcapped polyoxazolines can be prepared by polymerizing 2-ethyl-2-oxazoline onto a mixture of 3-vinylbenzyl and 4-benzylchlorides. See EXAMPLE III.

Also highly useful herein are endcapped polyalkylene glycol monoalkyl ether macromonomers corresponding to the following general chemical formula



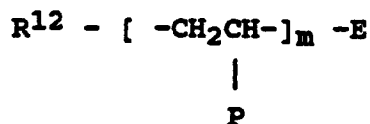
wherein R'' is selected from C1-C40 straight or branched chain alkyl, more preferably from C1-C8 straight or branched chain alkyl, most preferably from C1-C4 straight or branched chain alkyl, and most preferably methyl; R<sup>3</sup> is selected from hydrogen, methyl, ethyl, or n-propyl, more preferably from hydrogen or methyl, most preferably from H. E is a copolymerizable, ethylenically unsaturated moiety (i.e. the endcapping moiety). Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, isoprenyl, cyclohexyl, cyclopentyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, 1-propenyl, isobutenyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 3-vinylbenzyl, 4-vinylbenzyl, and mixtures thereof. In the above structure, m is as described previously, wherein m is preferably an integer from about 20 to about 2000, more preferably from about 30 to about 750, and most preferably from about 40 to about 500. It is to be understood that in the above structure, that when R<sup>3</sup> is other than hydrogen that

various isomers of the resulting macromonomer are possible depending upon the orientation of the individual glycol moieties. Therefore, the structure depicted above for these endcapped polyalkylene glycol monolkayl ethers is a general one that is not intended to limit these materials to any one particular isomeric structure.

Highly preferred examples of endcapped polyalkylene glycol monoalkyl ethers useful herein include acryloyl endcapped polyethylene glycol monomethyl ether, 3-vinylbenzoyl endcapped polyethylene glycol monomethyl ether, 4-vinylbenzoyl endcapped polyethylene glycol monomethyl ether, methacryloyl endcapped polyethylene glycol monomethyl ether, and mixtures thereof.

The endcapped polyalkylene glycol monoalkyl ethers can be synthesized from the polyalkylene glycol monoalkyl ether and the reactive or activated form of an endcapping group employing standard reaction procedures. Suitable activated endcapping groups include vinyl, allyl, 3-vinylbenzoyl, and 4-vinylbenzoyl halides (e.g. chlorides, bromides, and iodides), and the acid chlorides and bromides derived from acrylic acid, methacrylic acid, and ethacrylic acid. The polyalkylene glycol monoalkyl ether can be synthesized from the corresponding polyalkylene glycol using any of the alkylating agents well known in the art (e.g., methyl iodide, methyl bromide, diazomethane, methyl sulfate, ethyl iodide). Polyethylene glycols of various molecular weight ranges, as well as their methyl ethers are commercially available from Aldrich Chemical Company and Union Carbide Corporation. Alternatively, the polyalkylene glycols can be synthesized from the corresponding alkylene oxides and alkylene glycols using standard synthetic procedures (e.g., the acid or base catalyzed polymerization of alkylene oxides).

Also highly useful herein are endcapped hydrophilic nitrogen-containing macromonomer units copolymerizable with A corresponding to the formula



wherein E is a copolymerizable, ethylenically unsaturated moiety (i.e. the endcapping moiety). Preferred is when E is selected from the group

consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 2-vinyl benzyl  
3-vinyl benzyl, 4-vinyl benzyl, 2-vinylbenzoyl, 3-vinylbenzoyl, 4-  
vinylbenzoyl, 1-butenyl, isobutenyl, isoprenyl, cyclopentenyl,  
cyclohexenyl, and mixtures thereof. More preferred is when E is selected  
5 from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl,  
2-vinylbenzyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzoyl,  
and mixtures thereof. Most preferred is when E is selected from the group  
consisting of 2-vinylbenzyl, 3-vinylbenzoyl, 4-vinylbenzyl and mixtures  
thereof. R<sup>12</sup> is selected from the group consisting of hydrogen, C1-6  
10 straight or branched chain alkyl, benzyl, 1-phenyl substituted C2-6  
straight or branched chain alkyl, 1,1-diphenyl substituted C2-6 straight or  
branched chain alkyl, and mixtures thereof. More preferably R<sup>12</sup> is 1,1-  
diphenyl-4-methylpentyl. P is selected from the group consisting of 2-  
pyridyl, 3-pyridyl, 4-pyridyl, halogen substituted 2-, 3-, or 4-pyridyl, C1-4  
15 alkyl substituted 2-, 3-, or 4-pyridyl, 2-aminophenyl, 3-aminophenyl, 4-  
aminophenyl, 2-aminomethylphenyl, 3-aminomethylphenyl, 4-  
aminomethylphenyl, and pharmaceutically acceptable salts and  
quaternized derivatives thereof, and mixtures thereof. In the preceding  
structure, m is preferably an integer from about 10 to about 2000, more  
20 preferably from about 15 to about 300, and most preferably from about 20  
to about 250.

In the preceding structure it is found that pharmaceutically  
acceptable salts and quaternized derivatives are especially preferred  
because of their highly desired physical characteristics and solubility  
25 characteristics. By pharmaceutically acceptable salt as used herein is  
meant a salt that is generally regarded as safe for human use without  
undue risk of toxicity and other adverse effects. Nonlimiting examples of  
pharmaceutically acceptable salts of these materials include  
hydrochloride salts and hydrobromide salts. Nonlimiting examples of  
30 quaternized derivatives include alkyl quaternized derivatives wherein said  
alkyl group is a C1-30 straight or branched chain moiety, preferably a C1-  
4 straight or branched chain moiety, more preferably wherein said alkyl  
group is methyl or ethyl.

Highly preferred examples of these endcapped nitrogen containing  
35 macromonomers useful herein include acryloyl endcapped poly(2-, 3-, or

4-vinyl pyridine), acryloyl endcapped poly(2-, 3-, or 4-vinyl ethylsubstituted pyridine), methacryloyl endcapped poly(2-, 3-, or 4-vinyl pyridine), 2-, 3-, or 4-vinyl benzyl endcapped poly(2-, 3-, or 4-vinylpyridine), 2-, 3-, or 4-vinyl benzyl endcapped poly(2-, 3-, or 4-vinyl pyridine hydrochloride), 2-, 3-, or 4-vinyl benzyl endcapped poly(2-, 3-, or 4-vinyl methyl-quaternized pyridine), 2-, 3-, or 4-vinyl benzyl endcapped poly(4-dimethylaminomethylvinylbenzene), 2-, 3-, or 4-vinyl benzyl endcapped poly(alkyl-quaternized dimethylaminoethylvinylbenzene), and mixtures thereof.

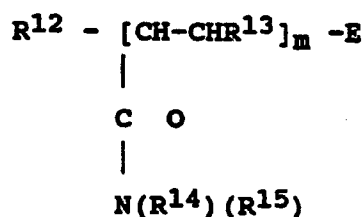
These nitrogen containing endcapped macromonomers can be synthesized using standard synthetic procedures which involve polymerizing, usually under anionic initiation conditions the appropriate monomer unit, (e.g. 2-, 3-, or 4- vinyl pyridine, 4-dimethylaminomethyl vinyl benzene, etc.). A wide variety of initiators can be used, nonlimiting examples of which include bases such as n-butyl lithium, sec-butyl lithium, t-butyl lithium, lithium aluminum hydride, sodium hydride, and the like. Nonlimiting examples of these bases are provided in Anionic Polymerization: Principles and Practice, Maurice Morton, Chapter 2, p. 13, Academic Press, N.Y. (1983), which is incorporated by reference herein in its entirety. It has been found especially convenient to use these strong bases in conjunction with sterically hindered hydrocarbon materials such as 1,1-diphenyl ethylene to generate a sterically hindered base for initiating the polymerization reaction, in which case, the sterically hindered hydrocarbon is the actual initiator, defined previously as "I", which is incorporated into the macromonomer structure. Once the desired degree of polymerization is achieved, an appropriate endcapping reagent is typically used to terminate the polymerization and to endcap the macromonomer., nonlimiting examples of these endcapping reagents include 2-vinylbenzyl chloride, 3-vinylbenzyl chloride, 4-vinylbenzyl chloride, and the like.

The pharmaceutically acceptable salts and quaternized derivatives of these nitrogen containing macromonomers are readily prepared from the macromonomers using standard synthetic procedures. Typically, the macromonomers are reacted with an acid to form the salt. For example reaction with hydrochloric acid or hydrobromic acid (either gaseous or as

an aqueous solution) would yield the corresponding hydrochloride and hydrobromide salts, respectively. To form the quaternized derivatives the macromonomers are reacted with a quaternizing agent. For example reaction with a methyl halide (e.g., methyl iodide, methyl chloride) or an alkyl sulfate (e.g. dimethyl sulfate, diethylsulfate) would yield the corresponding quaternized macromonomer.

More typically, the pharmaceutically acceptable salt or quaternized derivative of the thermoplastic elastomeric polymer is desired, in which case the non-salt form or non-quaternized macromonomer is incorporated into the thermoplastic elastomeric copolymer, followed by salt formation or quaternization of the copolymer using standard synthetic procedures analogous to those described for the macromonomer.

Also highly useful herein are endcapped hydrophilic polyacrylamide macromonomer units copolymerizable with A corresponding to the formula



wherein E is a copolymerizable, ethylenically unsaturated moiety (i.e. the endcapping moiety). Preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 2-vinyl benzyl, 3-vinyl benzyl, 4-vinyl benzyl, 2-vinylbenzoyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butentyl, isobutentyl, isoprenyl, cyclohexyl, cyclopententyl, cyclohexenyl, and mixtures thereof. More preferred is when E is selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, 2-vinylbenzyl, 3-vinylbenzyl, 4-vinylbenzyl, 3-vinylbenzoyl, 4-vinbenzoyl, and mixtures thereof. Most preferred is when E is selected from the group consisting of 2-vinylbenzyl, 3-vinylbenzyl, 4-vinylbenzyl and mixtures thereof. R<sup>12</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> straight or branched chain alkyl, benzyl, 1-phenyl substituted C<sub>2-6</sub> straight or branched chain alkyl, 1,1-diphenyl substituted C<sub>2-6</sub> straight or branched chain alkyl, and mixtures thereof.

R<sup>13</sup> is selected from the group consisting of H and C<sub>1-6</sub> straight or



branched chain alkyl, more preferably H and C<sub>1</sub>-C<sub>4</sub> straight or branched chain alkyl, and most preferably H, methyl, and ethyl. R<sup>14</sup>, and R<sup>15</sup> are independently selected from the group consisting of C<sub>1</sub>-8 straight or branched chain alkyl.; more preferably C<sub>1</sub>-6 straight or branched chain alkyl, and most preferably methyl. In the preceding structure, m is preferably an integer from about 10 to about 2000, more preferably from about 15 to about 3000, and most preferably from about 20 to about 250.

#### Polymers of the Present Invention

Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

N-butyl acrylate/2-methoxyethyl acrylate/Poly(4-dimethylimino methylvinyl benzene) 38/22/40

Methyl quaternized N-butyl acrylate/2-methoxyethyl acrylate/poly(4-dimethylaminomethylvinyl benzene) 38/22/40

Ethyl quaternized N-butyl acrylate/2-methoxyethyl acrylate/poly(2-vinylpyridine) 38/22/40

N-butyl acrylate/2-methoxyethyl acrylate/Poly(2-vinylpyridine) hydrochloride 38/22/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(N,N-dimethylacrylamide) 38/22/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(N,N-dimethylmethacrylamide) 38/22/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(2-ethyl-2-oxazoline) 38/22/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(2-ethyl-2-oxazoline)

38/22/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(2-ethyl-2-oxazoline)  
35/25/40

5 n-butyl acrylate/2-methoxyethyl acrylate/poly(2-ethyl-2-oxazoline)  
38/22/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(2-ethyl-2-oxazoline)  
38/22/40

n-butyl acrylate/poly(2-ethyl-2-oxazoline) 60/40

10 n-butyl acrylate/2-ethylhexyl methacrylate/poly(2-ethyl-2-oxazoline)  
40/20/40

n-butyl acrylate/2-methoxyethyl acrylate/poly(ethylene glycol) 386/22/40

15 n-butyl acrylate/2-(dimethylamino)ethyl methacrylate/poly(2-ethyl-2-oxazoline) 36/24/40

n-butyl acrylate/methyl quaternized 2-(dimethylamino)ethyl  
methacrylate/poly(2-ethyl-2-oxazoline) 36/24/40

#### Synthesis of the Copolymers

20 In general, the copolymers can be made by free radical polymerization of the A monomers with the B macromonomers. It is not intended to necessarily exclude from this invention any copolymers made by means other than free radical polymerization, so long as the product has the desired physical properties. The copolymers herein contain randomly repeating monomer units and macromonomer units.

25 The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers and macromonomers are all placed in a reactor, along with a

sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer and macromonomer loadings are from about 10% to about 50%, on a weight basis. Undesired terminators, especially oxygen, can be removed  
5 as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Nonlimiting examples of suitable initiators include those selected from the group consisting of azo initiators,  
10 peroxide initiators, redox initiators, and photochemical initiators. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further  
15 purified, as needed utilizing a variety of techniques including filtration, extraction, trituration, membrane separation, gel permeation chromatography, and like.

There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of  
20 degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers and macromonomer used, because different monomers and macromonomers have different solubilities and different reactivities to a specific initiator.

25 The copolymers of the present invention can also be synthesized by first preparing the backbone from the polymerization of suitable monomers, followed by further polymerization of the backbone with suitable hydrophilic monomers to form the polymeric side chains. This alternative procedure for synthesizing the copolymers herein is illustrated  
30 in EXAMPLE VII below.

When salts and/or quaternized polymers are desired, these polymers are readily prepared from the copolymers using standard procedures, such as reaction with a strong acid or a quaternizing agent. Preferred among the acids are hydrogen chloride and hydrogen bromide,  
35 which can be employed either as a gas or as an aqueous solution.

Commonly used quaternizing agents include alkyl halides (e.g., methyl iodide and methyl chloride) and alkyl and dialkyl sulfates (e.g., dimethyl sulfate and diethyl sulfate).

Analysis of the copolymer reaction product and the extracted materials, and the purified copolymer can be performed by conventional analysis techniques known in the art. These include, for example, nuclear magnetic resonance (NMR), infrared molecular spectroscopies, gel permeation/size exclusion chromatography, membrane osmometry, and atomic absorption and emission spectroscopies.

#### 10                    Hair Care and Topical Skin Care Compositions

The copolymers of the present invention can be formulated into a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos, conditioners, rinses, hand and body lotions, facial moisturizers, sunscreens, anti-acne preparations, topical analgesics, 15    mascaras, and the like. The carriers and additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the art. The following is a description of some of these carriers and additional components.

#### Carriers

#### 20                    Hair Care Compositions

The hair care compositions of the present invention can comprise a carrier, or a mixture of such carriers, which are suitable for application to the hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, more preferably from about 25    10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to the underlying skin.

Carriers suitable for use with hair care compositions of the present invention include, for example, those used in the formulation of hair 30    sprays, mousses, tonics, gels, shampoos, conditioners, and rinses. The choice of appropriate carrier will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic, or gel) or 35    rinsed off after use (e.g., shampoo, conditioner, rinse).

The carriers used herein can include a wide range of components conventionally used in hair care compositions. The carriers can contain a solvent to dissolve or disperse the particular copolymer being used, with water, the C1-C6 alcohols, and mixtures thereof being preferred; and water, methanol, ethanol, isopropanol, and mixtures thereof being more preferred. The carriers can also contain a wide variety of additional materials including, but not limited to acetone, hydrocarbons (such as isobutane, hexane, decene), halogenated hydrocarbons (such as Freons), linalool, esters (such as ethyl acetate, dibutyl phthalate), and volatile silicon derivatives (especially siloxanes such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, cyclomethicone, and dimethicone having for example, a viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. When the hair care composition is a hair spray, tonic, gel, or mousse the preferred solvents include water, ethanol, volatile silicone derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other. Mousses and aerosol hair sprays can also utilize any of the conventional propellants to deliver the material as a foam (in the case of a mousse) or as a fine, uniform spray (in the case of an aerosol hair spray). Examples of suitable propellants include materials such as trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilize an emulsifying agent. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. Fluorosurfactants are especially preferred, particularly if the product is a hair spray composition and most especially if it is a spray composition having relatively low levels of volatile organic solvents, such as alcohols, and relatively high levels of water (e.g., in excess of about 10%, by weight water). If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or cans having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAYR hair sprays.

Where the hair care compositions are conditioners and rinses the carrier can include a wide variety of conditioning materials. Where the hair care compositions are shampoos, the carrier can include surfactants, suspending agents, thickeners etc. Various additional components useful in hair care compositions are described in U.S. Patent No. 5,106,609, to Bolich, Jr. et al., issued April 21, 1992; and U.S. Patent No. 4,387,090, to Bolich, Jr. issued June 7, 1983; which are incorporated by reference herein. Some of these additional components are described below.

#### Topical Skin Care Compositions

The topical cosmetic and pharmaceutical compositions of the present invention can comprise a carrier. The carrier should be "cosmetically and/or pharmaceutically acceptable", which means that the carrier is suitable for topical application to the skin, has good aesthetic properties, is compatible with the copolymers of the present invention and any other components, and will not cause any untoward safety or toxicity concerns.

The carrier can be in a wide variety of forms. For example, emulsion carriers, including, but not limited to, oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions, are useful herein. These emulsions can cover a broad range of viscosities, e.g, from about 100 cps to about 200,000 cps. These emulsions can also be delivered in the form of sprays using either mechanical pump containers or pressurized aerosol containers using conventional propellants. These carriers can also be delivered in the form of a mousse. Other suitable topical carriers include

anhydrous liquid solvents such as oils, alcohols, and silicones (e.g., mineral oil, ethanol, isopropanol, dimethicone, cyclomethicone, and the like); aqueous-based single phase liquid solvents (e.g., hydro-alcoholic solvent systems); and thickened versions of these anhydrous and aqueous-based single phase solvents (e.g., where the viscosity of the solvent has been increased to form a solid or semi-solid by the addition of appropriate gums, resins, waxes, polymers, salts, and the like). Examples of topical carrier systems useful in the present invention are described in the following four references all of which are incorporated herein by reference in their entirety: "Sun Products Formulary" Cosmetics & Toiletries, vol. 105, pp. 122-139 (December 1990); "Sun Products Formulary", Cosmetics & Toiletries, vol. 102, pp. 117-136 (March 1987); U.S. Patent No. 4,960,764 to Figueroa et al., issued October 2, 1990; and U.S. Patent No. 4,254,105 to Fukuda et al., issued March 3, 1981.

The carriers of the skin care compositions can comprise from about 50% to about 99% by weight of the compositions of the present invention, preferably from about 75% to about 99%, and most preferably from about 85% to about 95%.

Preferred cosmetically and/or pharmaceutically acceptable topical carriers include hydro-alcoholic systems and oil-in-water emulsions. When the carrier is a hydro-alcoholic system, the carrier can comprise from about 1% to about 99% of ethanol, isopropanol, or mixtures thereof, and from about 1% to about 99% of water. More preferred is a carrier comprising from about 5% to about 60% of ethanol, isopropanol, or mixtures thereof, and from about 40% to about 95% of water. Especially preferred is a carrier comprising from about 20% to about 50% of ethanol, isopropanol, or mixtures thereof, and from about 50% to about 80% of water. When the carrier is an oil-in-water emulsion, the carrier can include any of the common excipient ingredients for preparing these emulsions. Additional components useful in formulating these topical compositions are further described below.

#### Additional Components

A wide variety of additional components can be employed in the hair care and topical skin compositions herein. Non-limiting examples include the following:

Pharmaceutical Actives

The compositions of the present invention, especially the topical skin care compositions, can comprise a safe and effective amount of a pharmaceutical active. The phrase "safe and effective amount", as used herein, means an amount of an active high enough to significantly or positively modify the condition to be treated, but low enough to avoid serious side effects (at a reasonable benefit/risk ratio), within the scope of sound medical judgement. A safe and effective amount of the pharmaceutical active will vary with the specific active, the ability of the composition to penetrate the active through the skin, the amount of composition to be applied, the particular condition being treated, the age and physical condition of the patient being treated, the severity of the condition, the duration of the treatment, the nature of concurrent therapy, and like factors.

The pharmaceutical actives which can be used in the compositions of the present invention preferably comprise from about 0.1% to about 20% by weight of the compositions, more preferably from about 0.1% to about 10%, and most preferably from about 0.1% to about 5%. Mixtures of pharmaceutical actives may also be used.

Nonlimiting examples of pharmaceutical actives can include the following:

Useful pharmaceutical actives in the compositions of the present invention include anti-acne drugs. Anti-acne drugs preferred for use in the present invention include the keratolytics such as salicylic acid, sulfur, lactic acid, glycolic, pyruvic acid, urea, resorcinol, and N-acetylcysteine; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); antibiotics and antimicrobials such as benzoyl peroxide, octopirox, erythromycin, zinc, tetracyclin, triclosan, azelaic acid and its derivatives, phenoxy ethanol and phenoxy propanol, ethylacetate, clindamycin and meclocycline; sebastats such as flavinoids; alpha and beta hydroxy acids; and bile salts such as scymnol sulfate and its derivatives, deoxycholate, and cholate. Preferred for use herein is salicylic acid.

Useful pharmaceutical actives in the compositions of the present invention include non-steroidal anti-inflammatory drugs (NSAIDS). The NSAIDS can be selected from the following categories: propionic acid



derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in the U.S. Patent 4,985,459 to Sunshine et al., issued January 15, 1991, incorporated by reference herein. Most preferred are  
5 the propionic NSAIDS including but not limited to aspirin, acetaminophen, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen, fenbufen, ketoprofen, indoprofen, pirprofen, carprofen, oxaprozin, pranoprofen, miroprofen, tioxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-  
10 inflammatory drugs including hydrocortisone and the like.

Useful pharmaceutical actives in the compositions of the present invention include antipruritic drugs. Antipruritic drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of methdilazine and trimeprazine. Useful  
15 pharmaceutical actives in the compositions of the present invention include include anesthetic drugs. Anesthetic drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexylcaine, procaine,  
20 cocaine, ketamine, pramoxine and phenol. Useful pharmaceutical actives in the compositions of the present invention include antimicrobial drugs (antibacterial, antifungal, antiprotozoal and antiviral drugs). Antimicrobial drugs preferred for inclusion in compositions of the present invention include pharmaceutically-acceptable salts of b-lactam drugs,  
25 quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, triclosan, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, metronidazole, pentamidine, gentamicin, kanamycin, lineomycin, methacycline, methenamine, minocycline, neomycin, netilmicin,  
30 paromomycin, streptomycin, tobramycin, miconazole and amantadine. Antimicrobial drugs preferred for inclusion in compositions of the present invention include tetracycline hydrochloride, erythromycin estolate, erythromycin stearate (salt), amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine gluconate, chlorhexidine  
35 hydrochloride, chlortetracycline hydrochloride, oxytetracycline

hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, 5 minocycline hydrochloride, neomycin sulfate, netilmicin sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amantadine hydrochloride, amantadine sulfate, triclosan, octopirox, parachlorometa xyleneol, nystatin, tolnaftate and clotrimazole.

10 Also useful herein are sunscreens agents. A wide variety of sunscreens agents are described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter 15 VIII, pages 189 et seq., of Cosmetics Science and Technology, all of which are incorporated herein by reference in their entirety. Preferred among those sunscreens which are useful in the compositions of the instant invention are those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 20 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof.

25 Still other useful sunscreens are those disclosed in U.S. Patent No. 4,937,370, to Sabatelli, issued June 26, 1990; and U.S. Patent No. 4,999,186, to Sabatelli et al., issued March 12, 1991; these two references are incorporated by reference herein in their entirety. The sunscreens agents disclosed therein have, in a single molecule, two 30 distinct chromophore moieties which exhibit different ultra-violet radiation absorption spectra. One of the chromophore moieties absorbs predominantly in the UVB radiation range and the other absorbs strongly in the UVA radiation range. These sunscreens agents provide higher efficacy, broader UV absorption, lower skin penetration and longer lasting 35 efficacy relative to conventional sunscreens. Especially preferred

examples of these sunscreens include those selected from the group consisting of 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2,4-dihydroxybenzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-hydroxydibenzoylmethane, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-(2-ethylhexyl)-methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof.

Generally, the sunscreens can comprise from about 0.5% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly used measure of photoprotection of a sunscreen against erythema. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

Also useful in the present invention are sunless tanning agents including dihydroxyacetone, glyceraldehyde, indoles and their derivatives, and the like. These sunless tanning agents may also be used in combination with the sunscreen agents.

Other useful actives include skin bleaching (or lightening) agents including but not limited to hydroquinone, ascorbic acid, kojic acid and sodium metabisulfite.

Other useful actives which are especially useful for hair care compositions include anti-dandruff actives such as zinc pyrithione, octopirox, selenium disulfide, sulfur, coal tar, and the like.

**Conditioners** Conditioning agents useful herein, and especially useful for hair care compositions, include hydrocarbons, silicone fluids, and cationic materials.

The hydrocarbons can be either straight or branched chain and can contain from about 10 to about 16, preferably from about 12 to about 16 carbon atoms. Examples of suitable hydrocarbons are decane, dodecane, tetradecane, tridecane, and mixtures thereof.

Silicone conditioning agents useful herein can include either cyclic or linear polydimethylsiloxanes, phenyl and alkyl phenyl silicones, and silicone copolyols. The linear volatile silicones generally have viscosities of less than about 5 centistokes at 25°C, while the cyclic materials have

viscosities less than about 10 centistokes.

Cationic conditioning agents useful herein can include quaternary ammonium salts or the salts of fatty amines. Preferred quaternary ammonium salts are dialkyl dimethyl ammonium chlorides, wherein the  
5 alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids. Representative examples of quaternary ammonium salts include ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, and di(hydrogenated tallow) ammonium chloride. Other quaternary  
10 ammonium salts useful herein are dicationics such as tallow propane diammonium dichloride. Quaternary imidazolinium salts are also useful herein. Examples of such materials are those imidazolinium salts containing C12-22 alkyl groups such as 1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4,  
15 5-dihydroimidazolinium chloride, 1-methyl-1-[(palmitoylamide)ethyl]-2-octadecyl-4,5-dihydroimidazolinium chloride and 1-methyl-1-[(tallowamide)-ethyl]-2-tallow-imidazolinium methyl sulfate. Also useful herein are salts of fatty amines. Examples of such compounds include stearylamine hydrochloride, soyamine hydrochloride, and stearylamine formate. Useful conditioning agents are disclosed in  
20 U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983, which is incorporated by reference herein.

#### Humectants and Moisturizers

The compositions of the present invention can contain one or more humectant or moisturizing materials. A variety of these materials can be  
25 employed and each can be present at a level of from about 0.1% to about 20%, more preferably from about 1% to about 10% and most preferably from about 2% to about 5%. These materials include urea; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary  
30 alkyl ammonium); aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycols; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; lactamide monoethanolamine;  
35 acetamide monoethanolamine; and mixtures thereof. Preferred

humectants and moisturizers are glycerol, butylene glycol, hexylene glycol, and mixtures thereof.

### Surfactants

The compositions of the present invention, especially the shampoo and conditioner compositions, can contain one or more surfactants. These surfactants are useful adjuncts for the carriers of the present compositions, and are not required for solubilizing or dispersing the copolymers of the present invention. For a shampoo, the level is preferably from about 10% to about 30%, preferably from 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants. A wide variety of surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to Mc Call et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; and U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992, all of which are incorporated by reference herein.

Nonlimiting examples of these surfactants include anionic surfactants such as alkyl and alkyl ether sulfates. These materials typically have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty

acids, for example, are derived from coconut oil. Still other anionic synthetic surfactants include the class designated as succinamates, olefin sulfonates having about 12 to about 24 carbon atoms, and b-alkyloxy alkane sulfonates. Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

Nonionic surfactants useful herein are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant. These nonionic surfactants can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Cationic surfactants useful in compositions of the present invention are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

Zwitterionic surfactants are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl

dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine, and amidobetaines and amidosulfobetaines (wherein the  $\text{RCONH}(\text{CH}_2)_3$  radical is attached to the nitrogen atom of the betaine).

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

#### Carboxylic Acid Copolymer Thickeners

Another component useful in the compositions herein is a carboxylic copolymer thickener. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol. The preferred polymers for use herein are of two general types. The first type of polymer is a crosslinked homopolymer of an acrylic acid monomer or derivative thereof (e.g., wherein the acrylic acid has substituents on the two and three carbon positions independently selected from the group consisting of  $\text{C}_{1-4}$  alkyl, -CN, -COOH, and mixtures thereof). The second

type of polymer is a crosslinked copolymer having a first monomer selected from the group consisting of an acrylic acid monomer or derivative thereof (as just described in the previous sentence), a short chain alcohol (i.e. a C<sub>1-4</sub>) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C<sub>1-4</sub> alkyl, -CN, -COOH, and mixtures thereof), and mixtures thereof; and a second monomer which is a long chain alcohol (i.e. C<sub>8-40</sub>) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C<sub>1-4</sub> alkyl, -CN, -COOH, and mixtures thereof). Combinations of these two types of polymers are also useful herein.

In the first type of crosslinked homopolymers the monomers are preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid being most preferred. In the second type of crosslinked copolymers the acrylic acid monomer or derivative thereof is preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid, methacrylic acid, and mixtures thereof being most preferred. The short chain alcohol acrylate ester monomer or derivative thereof is preferably selected from the group consisting of C<sub>1-4</sub> alcohol acrylate esters, C<sub>1-4</sub> alcohol methacrylate esters, C<sub>1-4</sub> alcohol ethacrylate esters, and mixtures thereof, with the C<sub>1-4</sub> alcohol acrylate esters, C<sub>1-4</sub> alcohol methacrylate esters, and mixtures thereof, being most preferred. The long chain alcohol acrylate ester monomer is selected from C<sub>8-40</sub> alkyl acrylate esters, with C<sub>10-30</sub> alkyl acrylate esters being preferred.

The crosslinking agent in both of these types of polymers is a polyalkenyl polyether of a polyhydric alcohol containing more than one alkenyl ether group per molecule, wherein the parent polyhydric alcohol contains at least 3 carbon atoms and at least 3 hydroxyl groups. Preferred crosslinkers are those selected from the group consisting of allyl ethers of sucrose and allyl ethers of pentaerythritol, and mixtures thereof. These polymers useful in the present invention are more fully



described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 4,509,949, to Huang et al., issued April 5, 1985; U.S. Patent No. 2,798,053, to Brown, issued July 2, 1957; which are incorporated by reference herein. See also, CTFA International  
5 **Cosmetic Ingredient Dictionary**, fourth edition, 1991, pp. 12 and 80; which are also incorporated herein by reference.

Examples of commercially available homopolymers of the first type useful herein include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerythritol. The carbomers  
10 are available as the Carbopol® 900 series from B.F. Goodrich. Examples of commercially available copolymers of the second type useful herein include copolymers of C<sub>10-30</sub> alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C<sub>1-4</sub>  
15 alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerythritol. These copolymers are known as acrylates/C<sub>10-30</sub> alkyl acrylate crosspolymers and are commercially available as Carbopol® 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich. In other words, examples of carboxylic acid polymer thickeners useful herein are  
20 those selected from the group consisting of carbomers, acrylates/C<sub>10-30</sub> alkyl acrylate crosspolymers, and mixtures thereof.

The compositions of the present can comprise from about 0.025% to about 1%, more preferably from about 0.05% to about 0.75% and most preferably from about 0.10% to about 0.50% of the carboxylic acid polymer thickeners.

#### 25 **Emulsifiers**

The compositions herein can contain various emulsifiers. These emulsifiers are useful for emulsifying the various carrier components of the compositions herein, and are not required for solubilizing or dispersing the copolymers of the present invention. Suitable emulsifiers  
30 can include any of a wide variety of nonionic, cationic, anionic, and zwitterionic emulsifiers disclosed in the prior patents and other references. See McCutcheon's, **Detergents and Emulsifiers**, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S.  
35 Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S.

Patent No. 3,755,560 to Dickert et al., issued August 28, 1973; these four references are incorporated herein by reference in their entirety.

Suitable emulsifier types include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable emulsifiers can include, but are not limited to, polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Ceteareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise from about 0.1% to about 10%, more preferably from about 1% to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

#### Emollients

The compositions useful in the methods of the present invention can also optionally comprise at least one emollient. Examples of suitable emollients include, but are not limited to, volatile and non-volatile silicone oils, highly branched hydrocarbons, and non-polar carboxylic acid and alcohol esters, and mixtures thereof. Emollients useful in the instant invention are further described in U.S. Patent No. 4,919,934, to Deckner et al., issued April 24 1990, which is incorporated herein by reference in its entirety.

The emollients can typically comprise in total from about 1% to about 50%, preferably from about 1% to about 25%, and more preferably from about 1% to about 10% by weight of the compositions useful in the present invention.

#### Additional Components

A variety of additional components can be incorporated into the compositions herein. Non-limiting examples of these additional

components include vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like); low pH thickening agents (e.g. polyacrylamide and C<sub>13-14</sub> isoparaffin and laureth-7, available as Sepigel from Seppic Corporation; polyquaternium and mineral oil, available as Salcare SC92, from Allied Colloids; crosslinked methyl quaternized dimethylaminomethacrylate and mineral oil, available as Salcare SC95 from Allied Colloids; resins; gums and thickeners such as xanthan gum, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, alkyl-modified hydroxyalkyl celluloses (e.g. long chain alkyl modified hydroxyethyl celluloses such as cetyl hydroxyethylcellulose), and magnesium aluminum silicate; cationic polymers and thickeners (e.g., cationic guar gum derivatives such as guar hydroxypropyltrimonium chloride and hydroxypropyl guar hydroxypropyltrimonium chloride, available as the Jaguar C series from Rhone-Poulenc; polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex<sup>R</sup> V-220); suspending agents such as ethylene glycol distearate and the like; preservatives for maintaining the antimicrobial integrity of the compositions; skin penetration aids such as DMSO, 1-dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.) and the like; antioxidants; chelators and sequestrants; and aesthetic components such as fragrances, colorings, essential oils, skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), pantothenic acid and its derivatives, clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisababol, dipotassium glycyrrhizinate and the like.

#### 30 Method of Using Hair and Skin Care Compositions

The hair care and skin care compositions of the present invention are used in conventional ways to provide the desired benefit appropriate to the product such as hair styling, holding, cleansing, conditioning and the like for hair care compositions and benefits such as moisturization, 35 sun protection, anti-acne, anti-wrinkling, artificial tanning, analgesic, and

other cosmetic and pharmaceutical benefits for skin care compositions. Such methods of use depend upon the type of composition employed but generally involve application of an effective amount of the product to the hair or skin, which may then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, or gel products), or allowed to remain on the skin (as in the case of the skin care compositions). By "effective amount" is meant an amount sufficient to provide the benefit desired. Preferably, hair rinse, mousse, and gel products are applied to wet or damp hair prior to drying and styling of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Cosmetic and pharmaceutical topical skin care compositions are applied to and rubbed into the skin.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

#### EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

Ingredients are identified by chemical or CTFA name.

#### EXAMPLE I

##### Synthesis of Poly(2-ethyl-2-oxazoline) Alcohol

To a solution of 50 g (0.5044 mol) of 2-ethyl-2-oxazoline in 50 mL of acetonitrile is added 0.92 g (0.0048 mol) of methyl-p-toluenesulfonate at 0 °C under a nitrogen atmosphere. The reaction mixture is heated at 80 °C for 20 hours and the resulting polymer solution is then refluxed with 2.3 mL distilled water in the presence of 5.6 g (0.0528 mol) of sodium carbonate for 24 hours. The solvents are removed under vacuum. The residue is extracted with 300 mL of dichloromethane for 24 hours, and the

insolubles are removed by suction filtration. The dichloromethane is then evaporated to yield about 48 g (96% yield) of poly(2-ethyl-2-oxazoline) alcohol.

#### EXAMPLE II

##### 5 Synthesis of Acrylate-Capped Poly(2-ethyl-2-oxazoline) Alcohol Macromonomer

To a solution of 48 g of poly(2-ethyl-2-oxazoline) alcohol (from EXAMPLE I) and 1.0 g (0.01056 mol) of triethylamine in 80 mL of dichloromethane is added dropwise a solution of 0.95 g (0.01056 mol) of acryloyl chloride at 0°C under a nitrogen atmosphere. The reaction mixture is then stirred at room temperature for 36 hrs, and the resulting solution is then suction filtered to remove the insolubles. The solvent and any unreacted triethylamine are removed by evaporation under vacuum. The resulting solid is then redissolved in 200 mL of dichloromethane, 10 filtered, and evaporated under vacuum to yield about 45.6 g (95% yield) of the macromonomer. 15

Using an analogous procedure the methacrylate and ethacrylate endcapped macromonomers are prepared by replacing the acryloyl chloride with an equivalent molar amount of methacryloyl chloride and ethacryloyl chloride, respectively. 20

#### EXAMPLE III

##### Synthesis of Vinylbenzyl-Capped Poly(2-ethyl-2-oxazoline) Alcohol Macromonomer

To a solution of 50 g (0.5044 mol) of 2-ethyl-2-oxazoline in 50 mL of acetonitrile is added a mixture of 0.3816 g (0.0025 mol) of meta and paravinylbenzylchlorides (available from Aldrich Chemical Co.), 0.562 g (0.0037 mol) of sodium iodide and 0.06 g (0.00023 mol) of N,N'-diphenyl-p-phenylenediamine. The solution is then heated at 90°C for 16 hours. To the resulting reaction product is added 100 mL of dichloromethane and the solution is filtered and then precipitated in 800 mL of ether. The precipitate product is collected by vacuum filtration and dried under vacuum at ambient temperature to yield about 45 g (90% yield) of the macromonomer. 25 30

#### EXAMPLE IV

##### 35 Synthesis of Acrylate-Capped Poly(ethylene glycol)methyl Ether

Macromonomer

To a solution of 50 g (0.01 mol) of poly(ethylene glycol)methyl ether having an average molecular weight of about 5000 (commercially available from Aldrich Chemical Co.) and 4.05 g (0.04 mol) of triethylamine in 400 mL of dichloromethane is added dropwise at 0°C under a nitrogen atmosphere a solution of 2.26 g (0.025 mol) of acryloyl chloride dissolved in 25 mL of dichloromethane. The reaction mixture is then stirred at room temperature for 36 hrs, and the resulting solution is then suction filtered to remove the insolubles. The solvent and any unreacted triethylamine are removed by evaporation under vacuum. The resulting solid is then redissolved in 300 mL of dichloromethane, filtered, and evaporated under vacuum to yield about 50 g (100% yield) of the macromonomer.

The above procedure is varied using other poly(ethylene glycol)alkyl ethers (e.g. methyl, ethyl, 2-ethylhexyl, decyl, dodecyl, cetyl, stearyl, lauryl, and myristyl wherein the polymer has an average molecular weight varying from about 1000 to about 200,000) to obtain the analogous acrylate-capped macromonomers. Additionally, the methacrylate and ethacrylate endcapped macromonomers are prepared by replacing the acryloyl chloride with an equivalent molar amount of methacryloyl chloride and ethacryloyl chloride, respectively.

EXAMPLE VSynthesis of Poly(n-butyl acrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer

To a solution of 16.0 g (0.1248 mol) of n-butyl acrylate, and 4 g of acrylate capped poly(2-ethyl-2-oxazoline) macromonomer (from Example II) in 100 mL of acetone is added 0.03 g (0.00018 mol) of azoisobutyronitrile (AIBN) initiator. The resulting solution is refluxed slowly for about 20 hours. The reaction is then quenched by the addition of about 5 mL of methanol. The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 18.4 g of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers and macromonomers used, this

procedure is used to prepare other copolymers of the present invention.

#### EXAMPLE VI

##### Synthesis of Poly(n-butyl-co-2-methoxyethylacrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer: Method I

- 5 To a solution of 4.5 g (0.035 mol) of n-butyl acrylate, 2.5 g (0.0192 mol) of 2-methoxy ethylacrylate and 3 g poly(2-ethyl-2-oxazoline) macromonomer (from Example II) in 40 mL of acetone is added 0.05 g of AIBN initiator. The resulting solution is refluxed slowly for about 20 hours. The reaction is then quenched by the addition of about 5 mL of methanol.
- 10 The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 9.5 g of the thermoplastic elastomeric copolymer.
- 15 Alternatively, by varying the monomers and macromonomers used, this procedure is used to prepare other copolymers of the present invention.

#### EXAMPLE VII

##### Synthesis of Poly(n-butyl-co-2-methoxyethylacrylate)-graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer: Method II

- 20 To a 500 mL round-bottomed flask is added 20.8 g (0.1623 mol) of n-butyl acrylate, 11.2 g (0.0861 mol) of 2-methoxyethyl acrylate, 0.30 g (0.002 mol) p-vinylbenzyl chloride, and 0.02 g (0.0012 mol) of azoisobutyronitrile (AIBN) initiator, in 200 mL of acetone. The resulting solution is refluxed slowly for about 24 hours. The reaction is then
- 25 quenched by the addition of about 5 mL of methanol and cooled to room temperature. The solvents are removed by rotary evaporation and the resulting polymer is dissolved in 250 mL of dry acetonitrile. Next 20.0 g (0.2018 mol) of 2-ethyl-2-oxazoline and 0.44 g (0.0029 mol) of sodium iodide is added and the solution is heated to 90 °C for 20 hours. The
- 30 resulting solution is filtered and the solvent is evaporated to yield about 45.0 g (86% yield) of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers used, this procedure is used to prepare other copolymers of the present invention.

#### EXAMPLE VIII

- 35 Synthesis of Poly(n-butyl-co-2-(dimethylamino)ethyl methacrylate)-

graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric

To a solution of 7.2 g (0.0561 mol) of *n*-butyl acrylate, 4.8 g (0.0305 mol) of 2-(dimethylamino)ethyl methacrylate, and 8.0 g poly(2-ethyl-2-oxazoline) macromonomer (from Example II) in 80 mL of acetone is added 0.01 g of AIBN initiator. The resulting solution is refluxed slowly for about 24 hours. The reaction is then quenched by the addition of about 5 mL of methanol. The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 18.4 g of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers and macromonomers used, this procedure is used to prepare other copolymers of the present invention.

EXAMPLE IX

Synthesis of Methyl Quaternized Poly(*n*-butyl-co-2-(dimethylamino)- ethyl methacrylate)graft-poly(2-ethyl-2-oxazoline) Thermoplastic Elastomeric Copolymer

To 10 grams of the copolymer from EXAMPLE VIII dissolved in 80 grams of ethanol is added dropwise 4.32 g (0.0281 mole) of dimethylsulfate. The resulting solution is stirred for 2 hours at room temperature. The solvent is removed by rotary evaporation to yield about 10 grams of the methyl quaternized copolymer.

EXAMPLE XHair Spray

Hair spray compositions are prepared from the following components utilizing conventional mixing techniques.

Ingredients

	<u>Weight %</u>			
	A	B	C	D
Water	QS 100	QS 100	QS 100	QS 100
Ethanol (SCA 40)	79.0	79.0	79.0	90.0
Copolymer of Example VI <sup>1</sup>	4.0	4.0	3.0	3.0
Fragrance	0.1	0.2	—	—

These products are prepared by first dissolving the polymer in the ethanol with stirring. The water and fragrance are then added with



stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray.

These hair sprays are useful for application to the hair to provide a styling and holding benefit.

<sup>1</sup> Alternatively, spray compositions are prepared using the copolymers of Examples V, VIII, XXII, XXIII, XXIV, and XXVI.

#### EXAMPLE XI

##### Reduced Volatile Organic Content Hairspray

Hair spray compositions are prepared from the following components utilizing conventional mixing techniques.

Ingredients	A	B	C	D
Water	QS 100	QS 100	QS 100	QS 100
Ethanol	54.0	54.0	54.0	54.0
Copolymer of Example VI <sup>1</sup>	4.0	3.0	4.0	3.0
Fragrance	0.05	0.2	—	—

These products are prepared by first dissolving the polymer in the ethanol with stirring. The water and fragrance are then added with stirring. The resulting hair spray compositions can then be packaged in a nonaerosol spray pump. Alternatively, the compositions can be combined with conventional propellants and packaged in an aerosol spray.

These hair sprays are useful for application to the hair to provide a styling and holding benefit.

<sup>1</sup> Alternatively, spray compositions are prepared using the copolymers of Examples V, VIII, XXII, XXIII, XXIV, and XXVI.

#### EXAMPLE XII

##### Mousse

Mousse compositions are prepared from the following components utilizing conventional mixing techniques.

Ingredients	Weight %
-------------	----------

	A	B	C
Water	QS 100	QS 100	QS 100
Copolymer of Example VIII <sup>1</sup>	3.00	2.50	3.50
Lauramide DEA	0.33	0.33	0.33
Sodium Methyl Oleyl Taurate	1.67	1.67	1.67
DMDM Hydantoin	0.78	0.78	0.78
Disodium EDTA	0.20	0.20	0.20
Polyoxyalkylated isostearyl alcohol <sup>2</sup>	0.10	0.10	0.10
Fragrance	0.10	0.10	0.10
Propellant <sup>3</sup>	7.0	7.0	7.0

These products are prepared by first dissolving the polymer in water with stirring. The remaining ingredients, except the propellant, are then added with stirring.

5 The resulting mousse concentrate can then be combined with conventional propellants (e.g., Propellant A46) and packaged in an aerosol spray.

These mousses are useful for application to the hair to provide a styling and holding benefit.

10 1 Alternatively, mousse compositions are prepared using the copolymers of Examples V, VI, XXII, XXIII, XXIV, and XXVI.

**2 Available as Aerosurf 66-E10.**

3 Available as a mixture of 82.46% isobutane, 16.57% propane, and 0.001% butane.

**15** **EXAMPLE XIII**

## Hair Tonic

Hair tonic compositions are prepared from the following components utilizing conventional mixing techniques.

Ingredients	Weight %		
	A	B	C
Ethanol	QS 100	QS 100	QS 100
Copolymer of Example VI <sup>1</sup>	0.75	1.00	1.25
Fragrance	0.10	0.20	0.30

These products are prepared by dissolving the polymer in the ethanol with stirring and then adding the fragrance and any colors.

These hair tonics are useful for application to the hair to provide a styling and holding benefit.

- 5 1 Alternatively, tonic compositions are prepared using the copolymers of Examples V, VIII, XXII, XXIII, XXIV, and XXVI.

#### EXAMPLE XIV

##### Hair Conditioner

- 10 A hair conditioner composition is prepared from the following components utilizing conventional mixing techniques.

##### Ingredient

##### Weight %

##### Styling Agent Premix

Copolymer of Example IX	1.00
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##### Silicone Premix

15 Silicone gum, GE SE76 <sup>1</sup>	0.30
Octamethyl cyclotetrasiloxane	1.70

##### Main Mix

Water	QS100
Cetyl Alcohol	1.00
20 Quaternium 18 <sup>2</sup>	0.85
Stearyl Alcohol	0.70
Hydroxethyl cellulose	0.50
Ceteareth-20	0.35
Fragrance	0.20
25 Dimethicone copolyol	0.20
Citric Acid	0.13
Methylchloroisothiazolinone (and)	
methylisothiazolinone	0.04
Sodium Chloride	0.01

- 30 The product is prepared by comixing all the Main Mix ingredients,

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heating to about 60°C with mixing, and colloid milling while cooling to about 45°C. At this temperature, the two premixes are added separately with moderate agitation and the resultant conditioner is allowed to cool to room temperature.

5 This product is useful as a rinse off hair conditioner.

<sup>1</sup> Commercially available from General Electric.

<sup>2</sup> Dimethyl Di(Hydrogenated Tallow) Ammonium Chloride

### EXAMPLE XV

#### Shampoo Composition

10 A shampoo composition is prepared from the following components utilizing conventional mixing techniques.

#### Ingredients

#### Weight %

#### Styling Agent

Copolymer from Example IX	1.00
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#### 15 Premix

Silicone gum	0.50
--------------	------

Dimethicone, 350 cs fluid	0.50
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#### Main Mix

Water	QS100
-------	-------

20 Ammonium lauryl sulfate	11.00
----------------------------	-------

Cocamide MEA	2.00
--------------	------

Ethylene glycol distearate	1.00
----------------------------	------

Xanthan Gum	1.20
-------------	------

Methylchloroisothiazolinone (and)	
-----------------------------------	--

25 methylisothiazolinone	0.04
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Citric Acid to pH 4.5 as needed

The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150°F with agitation for 1/2 hour.

The Styling Agent and the Premix are then added sequentially with about 10 minutes of agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either  
5 or both high shear mixing (high speed dispersator) or normal agitation.

This shampoo is useful for cleansing the hair and for providing a styling benefit.

#### Example XVI

##### Anti-Acne Composition

10 An anti-acne composition is made by combining the following components using conventional mixing technology.

<u>Ingredient</u>	<u>Weight %</u>
Water	QS100
Salicylic Acid	2.0
15 Copolymer from Example VI <sup>1</sup>	2.0
Ethanol (SDA 40)	40.0

The composition displays skin penetration of the salicylic acid as well as improved skin feel and residue characteristics and is useful for the treatment of acne.

20 1 Alternatively, the anti-acne compositions are prepared using the copolymers of Examples VIII, IX, XXII, XXIII, XXIV, and XXVI.

Example XVIITopical Analgesic Composition

A topical analgesic composition is made by combining the following ingredients utilizing conventional mixing techniques.

5	<u>Ingredient</u>	<u>Weight %</u>
	Water, Purified	QS100
	Ibuprofen	2.0
	Copolymer from Example VI <sup>1</sup>	2.0
	Ethanol (SDA 40)	20.0

- 10 The compositions display skin penetration of the ibuprofen active as well as improved skin feel and residue characteristics together with excellent moisturizing, emolliency, rub-in and absorption characteristics.

- 1 Alternatively, the topical analgesic compositions are prepared using the copolymers of Examples VIII, IX, XXII, XXIII, XXIV, and  
15 XXVI.

Example XVIIISunless Tanning Composition

A composition for sunless tanning is made by combining the following ingredients utilizing conventional mixing techniques.

20	<u>Ingredients</u>	<u>Weight %</u>
	<u>Phase A</u>	
	Water	qs 100
	Copolymer from Example VI <sup>1</sup>	2.00
	Carbomer 934 <sup>2</sup>	0.20
25	Carbomer 980 <sup>3</sup>	0.15
	Acrylic Acid Copolymer <sup>4</sup>	0.15
	<u>Phase B</u>	
	PPG-20 Methyl Glucose Ether	
	Distearate	2.00
30	Tocopheryl Acetate	1.20

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	Mineral Oil	2.00
	Stearyl Alcohol	1.00
	Shea Butter	1.00
	Cetyl Alcohol	1.00
5	Ceteareth-20	2.50
	Ceteth-2	1.00
	Ceteth-10	1.00
	<u>Phase C</u>	
10	DEA-Cetyl Phosphate	0.75
	<u>Phase D</u>	
	Dihydroxyacetone	3.00
	<u>Phase E</u>	
	Butylene Glycol	2.00
15	DMDM Hydantoin (and)	
	Iodopropynyl Butylcarbamate	0.25
	<u>Phase F</u>	
	Fragrance	1.00
	Cyclomethicone	2.00

- 20 In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85° C. In a separate vessel the Phase B ingredients are combined and heated to 85-90° C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The emulsion is
- 25 cooled to 40-45° C with continued mixing. Next, in a separate vessel, the dihydroxyacetone is dissolved in water and the resulting solution is mixed into the emulsion. In another vessel, the Phase E ingredients are heated with mixing to 40-45° C until a clear solution is formed and this solution is then added to the emulsion. Finally, the Phase F ingredients are added
- 30 to the emulsion with mixing, which is then cooled to 30-35° C, and then to room temperature.

This emulsion is useful for topical application to the skin to provide an artificial tan.

- 1 Alternatively, the artificial tanning compositions are prepared using the copolymers of Examples VIII and IX.
- 5 2 Available as Carbopol<sup>R</sup> 934 from B.F. Goodrich.
- 3 Available as Carbopol<sup>R</sup> 980 from B.F. Goodrich.
- 4 Available as Pemulen TR1 from B.F. Goodrich.

### EXAMPLE XIX

#### Sunscreen Composition

- 10 An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredients</u>	<u>Weight %</u>
	<u>Phase A</u>	
	Water	QS100
15	Carbomer 954 <sup>1</sup>	0.24
	Carbomer 1342 <sup>2</sup>	0.16
	Copolymer from Example VI <sup>3</sup>	1.75
	Disodium EDTA	0.05
	<u>Phase B</u>	
20	Isoarachidyl Neopentanoate <sup>4</sup>	2.00
	PVP Eicosene Copolymer <sup>5</sup>	2.00
	Octyl Methoxycinnamate	7.50
	Octocrylene	4.00
	Oxybenzone	1.00
25	Titanium Dioxide	2.00
	Cetyl Palmitate	0.75
	Stearoxytrimethylsilane	
	(and) Stearyl Alcohol <sup>6</sup>	0.50
	Glyceryl Tribehenate <sup>7</sup>	0.75
30	Dimethicone	1.00



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Tocopheryl Acetate	0.10
DEA-Cetyl Phosphate	0.20

Phase C

Water	2.00
5 Triethanolamine 99%	0.60

Phase D

Water	2.00
Butylene Glycol	2.00
DMDM Hydantoin (and)	
10 Iodopropynyl Butylcarbamate <sup>8</sup>	0.25
dL Panthenol	1.00

Phase E

Cyclomethicone	1.00
----------------	------

- 1 Available as Carbopol<sup>R</sup> 954 from B.F. Goodrich.  
 15 2 Available as Carbopol<sup>R</sup> 1342 from B.F. Goodrich.  
 3 Alternatively, the sunscreen compositions are prepared using the copolymers of Examples VIII and IX.  
 4 Available as Elefac I-205 from Bernel Chemical.  
 5 Available as Ganex V-220 from GAF Corporation.  
 20 6 Available as DC 580 Wax from Dow Corning.  
 7 Available as Synchrowax HRC from Croda.  
 8 Available as Glydant Plus from Lonza.

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45°C with continued mixing. In another vessel, the Phase D

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ingredients are heated with mixing to 40–45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35°C and the Phase E ingredient is added and mixed.

- 5 This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

### EXAMPLE XX

#### Facial Moisturizer

- 10 A leave-on facial emulsion composition containing a cationic hydrophobic surfactant is prepared by combining the following components utilizing conventional mixing techniques.

	<u>Ingredient</u>	<u>Weight %</u>
	Water	QS100
	Copolymer from Example VI <sup>1</sup>	1.00
15	Glycerin	3.00
	Cetyl Palmitate	3.00
	Cetyl Alcohol	1.26
	Quaternium-22	1.00
	Glyceryl Monohydroxy Stearate	0.74
20	Dimethicone	0.60
	Stearic Acid	0.55
	Octyldodecyl Myristate	0.20
	Carbomer 1342	0.125
	Tetrasodium EDTA	0.10
25	DMDM Hydantoin and Iodopropynyl	
	Butyl Carbamate	0.10
	Carbomer 951	0.075

This emulsion is useful for application to the skin as a moisturizer.

- 1 Alternatively, the moisturizers are prepared using the copolymers of  
30 Examples VIII, IX, XXII, XXIII, XXIV, and XXVI.

### EXAMPLE XXI

Styryl Capped Poly(2-vinyl pyridine) Macromonomer.

Approximately 800 mL of dry tetrahydrofuran is placed in a round bottom flask equipped with a mechanical stirrer and a thermometer and is cooled to -78°C using a dry ice/isopropanol bath. Next 7.69 grams (0.01 mole) of sec-butyl lithium (1.3 Molar solution in hexane) and 1.89 grams (0.0124 mole) of diphenylethylene are added. The mixture is then allowed to stir for 5 minutes. Next, 2-vinyl pyridine (105 grams, 1.0 moles) is added dropwise with stirring. After the addition is complete, 2.29 grams (0.15 mole) of para-vinyl benzyl chloride is added, and the reaction mixture is allowed to warm to room temperature with stirring. The reaction product is then carefully poured into 1 liter of n-hexanes solvent to precipitate the macromonomer. The macromonomer is isolated by suction filtration followed by drying under vacuum to yield 97.0 grams (92% yield) of styryl capped poly(2-vinyl pyridine) macromonomer.

Using the above procedure, the following monomers are used to prepare their corresponding macromonomers: 3-vinylpyridine, 4-vinylpyridine, 4-vinyl aminomethylbenzene, 4-vinyl dimethylaminomethylbenzene, 2-vinyl-5-chloropyridine, 2-vinyl-4-methylpyridine, and 4-vinyl dimethylaminoethylbenzene.

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EXAMPLE XXIISynthesis Of Poly(n-Butyl Acrylate-Co-2-Methoxyethylacrylate)-Graft-Poly(2-Vinylpyridine)

To a solution of 16.0 g (0.1248 mol) of n-butyl acrylate, and 4 g of styryl capped poly(2-vinyl pyridine) macromonomer (from Example XI) in 100 mL of acetone is added 0.03 g (0.00018 mol) of azoisobutyronitrile (AIBN) initiator. The resulting solution is refluxed slowly for about 20 hours. The reaction is then quenched by the addition of about 5 mL of methanol. The solution is then poured into a teflon pan and the acetone is evaporated at room temperature under a fume hood. The resulting polymer film is redissolved in ethanol, filtered, and the ethanol is then evaporated to yield about 18.4 g of the thermoplastic elastomeric copolymer.

Alternatively, by varying the monomers and macromonomers used, this procedure is used to prepare other copolymers of the present invention.

**EXAMPLE XXIII****Synthesis Of Methyl Quaternized Polymer Of Example XII**

To 5 grams of the copolymer from example XXII dissolved in 80  
5 grams of ethanol is added dropwise 2.16 grams (0.0140 mole) of  
dimethylsulfate. The resulting solution is stirred for 2 hours at room  
temperature. The solvent is removed by rotary evaporation to yield the  
methyl quaternized copolymer.

**EXAMPLE XXIV****Synthesis Of Hydrochloride Salt Of Polymer Of Example XXII**

To 5 grams of the copolymer from Example XXII dissolved in 80  
grams of ethanol is bubbled in hydrogen chloride gas for approximately  
15 minutes. The solvent is removed by rotary evaporation to yield the  
hydrochloride salt of the copolymer.

**EXAMPLE XXV****Styryl Capped Poly(N,N-Dimethylacrylamide)**

Using the procedure of Example XXI, 99 grams, (1.0 mole) of N,N-  
20 dimethylacrylamide is used instead of 2-vinylpyridine.

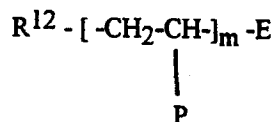
In an alternative procedure, the corresponding styryl capped  
poly(N,N-dimethylmethacrylamide) is prepared using N,N-  
dimethylmethacrylamide.

**EXAMPLE XXVI****Synthesis Of Poly(n-Butyl Acrylate-Co-2-Methoxyethylacrylate)-Graft-  
[Poly(2-N,N-Dimethylacrylamide)]**

Using the method of Example XXII, 4.0 grams of styryl capped  
poly(N,N-dimethylacrylamide) is used to replace the styryl capped poly(2-  
30 vinylpyridine).

What is Claimed is:

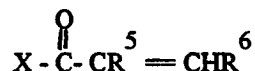
1. A water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and two or more polymeric side chains, said copolymer formed from the copolymerization of randomly repeating A and B units wherein said copolymer comprises:
  - (i) from 40% to 90% by weight of said A units, wherein said A units are polymerizable monomer units; and
  - (ii) from 10% to 60% by weight of said B units, wherein said B units are hydrophilic macromonomer units, copolymerizable with A, whereby said macromonomer units form said polymeric side chains; and wherein said B macromonomer units are selected from nitrogen containing macromonomers represented by the following structure



wherein R<sup>12</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> straight or branched chain alkyl, benzyl, and mixtures thereof, m is an integer from 10 to 2000; E is an ethylenically unsaturated moiety, copolymerizable with A, selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 2-vinyl benzyl, 3-vinyl benzyl, 4-vinyl benzyl, 2-vinylbenzoyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, isobutenyl, isoprenyl, cyclopentenyl, cyclohexenyl, and mixtures thereof; and P is selected from the group consisting of 2-pyridyl, 3-pyridyl, 4-pyridyl, 4-dimethylaminomethyl benzene, 4-aminomethyl benzene, 4-dimethylaminoethyl benzene, 4-aminoethyl benzene, and pharmaceutically acceptable salts and C<sub>1</sub>-C<sub>4</sub> alkyl quaternized derivatives thereof, and mixtures thereof;

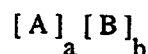
wherein said copolymer has a weight average molecular weight greater than 10,000, and wherein said copolymer exhibits two distinct T<sub>g</sub> values, said first T<sub>g</sub> corresponding to said backbone and having a value less than 0°C, and said second T<sub>g</sub> corresponding to said polymeric side chains and having a value greater than 25 °C.

2. A copolymer according to Claim 1 wherein R<sup>12</sup> is 1,1-diphenyl-4-methylpentyl and m is an integer from 20 to 250, and wherein P is selected from the group consisting of 2-pyridyl, 3-pyridyl, 4-pyridyl, hydrochloride and hydrobromide salts thereof, and methyl and ethyl quaternized derivatives thereof, and mixtures thereof, preferably wherein P is methyl quaternized 2-pyridyl.
3. A copolymer according to Claim 2 wherein the T<sub>c</sub> corresponding to said backbone is from -45°C to -120°C, and the T<sub>g</sub> corresponding to said hydrophilic polymeric side chains is from 35°C to 150°C.
4. A copolymer according to Claim 3 wherein said A monomer units comprise from 50% to 85% by weight of the total copolymer and said B macromonomer units comprise from 15% to 50% by weight of the total copolymer, preferably wherein said A monomer units comprise from 60% to 80% by weight of the total copolymer and said B macromonomer units comprise from 20% to 40% by weight of the total copolymer.
5. A copolymer according to Claim 4 wherein said A monomer units are of the formula



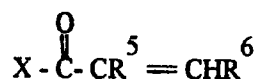
wherein X is selected from the group consisting of -OH, -OM, -OR<sup>4</sup>, -NH<sub>2</sub><sup>4</sup>, -NHR<sup>4</sup>, and -N(R<sup>2</sup>)<sub>2</sub>; M is a cation selected from the group consisting of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Zn<sup>++</sup>, NH<sub>4</sub><sup>+</sup>, alkylammonium, dialkylammonium, trialkylammonium, and tetralkylammonium; R<sup>4</sup> is selected from the group consisting of H, C<sub>1-8</sub> straight or branched chain alkyl, N,N-dimethylaminoethyl, methyl quaternized N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R<sup>5</sup> and R<sup>6</sup> are independently selected from the group consisting of H, C<sub>1-8</sub> straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; preferably wherein said A monomer units are selected from the group consisting of *n*-butyl acrylate, 2-ethylhexyl acrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, methyl quaternized N,N-dimethylaminoethyl acrylate, and mixtures thereof.

6. A water or alcohol soluble or dispersible thermoplastic elastomeric copolymer having a backbone and one or more polymeric side chains. said copolymer formed from the copolymerization of randomly repeating A and B units and corresponding to the formula



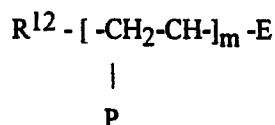
wherein

- (i) A is at least one polymerizable monomer unit corresponding to the formula



wherein X is selected from the group consisting of -OH, -OM, -OR<sup>4</sup>, -NH<sub>2</sub><sup>4</sup>, -NHR<sub>2</sub><sup>4</sup>, and -N(R<sub>2</sub>)<sub>2</sub><sup>4</sup>; M is a cation selected from the group consisting of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Zn<sup>++</sup>, NH<sub>4</sub><sup>+</sup>, alkylammonium, dialkylammonium, trialkylammonium, and tetralkylammonium; each R<sup>4</sup> is selected from the group consisting of H, C<sub>1-8</sub>-C straight or branched chain alkyl, N,N<sub>5</sub>-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl; and R<sub>6</sub> and R' are independently selected from the group consisting of H, C<sub>1-8</sub>-C straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl, and 2-ethoxyethyl; preferably wherein said A monomer units are selected from the group consisting of n-butyl acrylate, 2-ethylhexyl acrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, and mixtures thereof; R is methyl, R' is ethyl, m is an integer from 10 to 2000, a is an integer from 100 to 3000, and b is an integer from 2 to 50;

- (ii) B is at least one hydrophilic nitrogen containing macromonomer unit copolymerizable with A corresponding to the formula



wherein  $R^{12}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_6$  straight or branched chain alkyl benzyl, and mixtures thereof,  $m$  is an integer from 10 to 2000;  $E$  is an ethylenically unsaturated moiety, copolymerizable with  $A$  and  $C$ , selected from the group consisting of vinyl, allyl, acryloyl, methacryloyl, ethacryloyl, styryl, 2-vinyl benzyl, 3-vinyl benzyl, 4-vinyl benzyl, 2-vinylbenzoyl, 3-vinylbenzoyl, 4-vinylbenzoyl, 1-butenyl, isobutenyl, isoprenyl, cyclopentyl, cyclohexenyl, and mixtures thereof, and  $P$  is selected from the group consisting of 2-pyridyl, 3-pyridyl, 4-pyridyl, 4-dimethylaminoethyl benzene, 4-aminoethyl benzene, 4-dimethylaminoethyl benzene, 4-aminoethyl benzene, and pharmaceutically acceptable salts and  $C_1$ - $C_4$  alkyl quaternized derivatives thereof, and mixtures thereof; and

(iii)  $a$  is an integer of 100 or greater and  $b$  is an integer of 2 or greater; and wherein said copolymer exhibits two distinct  $T_g$  values, said first  $T_g$  corresponding to said backbone and having a value less than  $0^\circ\text{C}$ , and said second  $T_g$  corresponding to said polymeric side chains and having a value greater than  $25^\circ\text{C}$ .

7. A hair care composition useful for styling hair, comprising the copolymer of Claim 1 and a carrier suitable for application to the hair.
8. A hair care composition according to Claim 7, in the form of a liquid suitable for application to the hair, wherein said carrier comprises water, a  $C_1$ - $C_6$  monohydric alcohol, or a mixture thereof, preferably wherein said carrier further comprises a propellant.
9. A hair care composition according to Claim 7, in the form of a mousse for application to the hair, wherein said carrier comprises water, one or more surfactants, and a propellant.
10. A composition for topical application to the skin comprising the copolymer of Claim 1 and a carrier suitable for application to the skin.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/07385

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F290/04 A61K7/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER SCIENCE, vol.34, no.5, May 1992 pages 380 - 383 S.I. KLENIN 'molecular structure ...'	1-4
X	WO,A,92 09644 (BAUSCH & LOMB INC.) 11 June 1992 see page 8, line 3 - line 6; claims 1,3,8-10; examples 4-5	1
A	DATABASE WPI Section Ch, Week 9304, Derwent Publications Ltd., London, GB; Class A14, AN 93-032171 'copolymer cosmetic ...' & JP,A,4 359 914 (KAO CORP.) 14 December 1994 see abstract	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
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 "&" document member of the same patent family

Date of the actual completion of the international search

7 October 1994

Date of mailing of the international search report

11. 11. 94

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Inter- national Application No  
PCT/US 94/07385

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO,A,91 15186 (PROCTER &amp; GAMBLE) 17  October 1991  see claims 1,88; example IV  -----</p>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/07385

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9209644	11-06-92	US-A-	5219965	15-06-93
		CA-A-	2095045	28-05-92
		CN-A-	1061785	10-06-92
		EP-A-	0559809	15-09-93
		JP-T-	6503373	14-04-94
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WO-A-9115186	17-10-91	US-A-	5120531	09-06-92
		AU-A-	7674291	30-10-91
		CN-A-	1056053	13-11-91
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Publication number: **0 412 704 A2**

12

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54 Hair conditioning and styling compositions.

57 Hair care compositions which provide improved styling and hair conditioning properties are disclosed. The compositions comprise from about 0.1% to about 10.0% of a specifically-defined silicone copolymer and from about 0.5% to about 99.5% of a carrier suitable for application to hair. These compositions are characterized by the fact that, when dried, the polymer phase separates into a discontinuous phase which includes a silicone macromer and a continuous phase which includes the copolymer backbone.

**EP 0 412 704 A2**

## HAIR CONDITIONING AND STYLING COMPOSITIONS

TECHNICAL FIELD

This application is a continuation-in-part of U.S. Application Serial No. 390,568, Bolich and Torgerson,  
 5 filed August 7, 1989.

The present invention relates to hair care compositions which have improved hair conditioning and style retention properties while still leaving the hair with a natural non-sticky feel. These compositions utilize a group of specific silicone macromer-containing copolymers.

10

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally  
 15 accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of  
 20 mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following , shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has now been discovered that hair care compositions comprising certain specifically-defined silicone macromer-containing copolymers provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays, tonics, lotions, gels, and mousses. The compositions provide these benefits to hair without leaving the hair with a stiff or sticky/tacky feel and without negatively affecting dry hair  
 30 properties, such as ease of combing. Further, hair to which the compositions of the present invention have been applied may be restyled several times without requiring reapplication of the compositions.

The results are surprising since other materials which have been typically used in hair care compositions to provide style retention, such as resins and gums, generally hurt dry hair properties (e.g., combing) and leave hair with a sticky and/or stiff feel. Furthermore, silicone materials typically used for hair  
 35 conditioning tend to hurt style retention.

Siloxanes (see, for example, U.S. Patent 3,208,911, Oppliger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. U.S. Patent 4,601,902, Fridt et al., issued July 22, 1986, describes hair conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and  
 40 a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. U.S. Patent 4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. U.S. Patent 4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include  
 45 siloxane components containing substituents to provide attachment to hair. Japanese Published Application 56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxane oxyalkylene copolymer together with an acrylic resin. U.S. Patent 4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes).  
 50 Polyether-modified polysiloxanes are also disclosed for use in shampoos in U.S. Patent 3,957,970, Korkis, issued May 18, 1976. U.S. Patent 4,185,087, Morlino, issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties.

Siloxane-derived materials have also been used in hair styling compositions. Japanese Published Application 56-092,811, Lion Corporation, published December 27, 1979, describes hair setting composi-

tions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. U.S. Patent 4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which  
 5 include polydiorganosiloxanes and a cationic organic polymer are taught in U.S. Patent 4,733,677, Gee et al., issued March 29, 1988, and U.S. Patent 4,724,851, Cornwall et al., issued February 16, 1988. Finally, European Patent Application 117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid.

10 Siloxane-containing polymers have also been used in non-hair care applications. U.S. Patent 4,136,250, Mueller et al., issued January 23, 1979, relates to polymeric materials used in biological contexts where oxygen permeable and tissue compatible membranes are required. They can also be used as carriers for biologically-active substances. These materials are hydrophilic water-insoluble gels which include a low molecular weight terminal olefinic siloxane macromer and a polymer containing water-soluble monoolefinic  
 15 adhesive compositions which include a copolymer with a vinyl polymeric backbone having grafted thereto polysiloxane moieties. U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, describes pressure sensitive release coating compositions which comprise polysiloxane-grafted copolymers and blends of those copolymers with other polymeric materials. None of these last three patents suggest the use of the  
 20 disclosed siloxane-containing polymers in hair care compositions.

It is an object of the present invention to formulate hair care compositions which provide effective hair conditioning and style retention properties.

It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention from a single composition.

25 It is a further object of the present invention to formulate hair care compositions which provide good style retention without leaving hair with a stiff or sticky/tacky feel.

It is a further object of the present invention to provide an improved method for styling and conditioning hair.

These and other objects will become readily apparent from the detailed description which follows.

30 Unless otherwise indicated, all percentages and ratios herein are by weight.

### SUMMARY OF THE INVENTION

35

The present invention relates to hair care compositions comprising

(a) from about 0.1% to about 10.0% of a copolymer, having a molecular weight of from about 10,000 to about 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising C monomers and components selected from the group  
 40 consisting of A monomers, B monomers, and mixtures thereof wherein:

A is at least one free radically polymerizable vinyl monomer, the amount by weight of A monomer, when used, being up to about 98% of the total weight of all monomers in said copolymer;

B is at least one reinforcing monomer copolymerizable with A, the amount by weight of B monomer, when used, being up to about 98% of the total weight of all monomers in said copolymer, said B  
 45 monomer being selected from the group consisting of polar monomers and macromers, preferably having a T<sub>g</sub> or a T<sub>m</sub> above about -20° C; and

C is a polymeric monomer having a molecular weight of from about 1,000 to about 50,000 and the general formula

$X(Y)_nSi(R)_{2-m}(Z)_m$  wherein

50 X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl  
 55 polymeric backbone after copolymerization

n is 0 or 1

m is an integer from 1 to 3

wherein C comprises from about 0.01% to about 50% of the copolymer;

(b) from about 0.5% to about 99.5% of a carrier suitable for application to hair.

In another embodiment, the hair care compositions of the present invention include specifically-defined phase separating copolymers of silicone with a non-silicone adhesive polymer, preferably these compositions comprise

- 5 (a) from about 0.1% to about 10.0% of a silicone-containing copolymer having a vinyl polymeric backbone, preferably having a  $T_g$  above about  $-20^\circ\text{C}$ , and having grafted to the backbone a polydimethylsiloxane macromer having a weight average molecular weight between about 1,000 and about 50,000; and
- (b) from about 0.5% to about 99.5% of a carrier suitable for application to hair;
- 10 the polymer and carrier selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.

15

## DETAILED DESCRIPTION OF THE INVENTION

The essential, as well as the optional, components of the present invention are described below.

20

### Silicone-Containing Copolymer

The compositions of the present invention contain from about 0.1% to about 10.0%, preferably from  
 25 about 0.5% to about 8.0%, of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers should have a weight average molecular weight of from about 10,000 to about 1,000,000 (preferably from about 30,000 to about 300,000) and, preferably, have a  $T_g$  of at least about  $-20^\circ\text{C}$ . As used herein, the abbreviation " $T_g$ " refers to the glass transition temperature of the non-silicone backbone, and the  
 30 abbreviation " $T_m$ " refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

In its broadest sense, the polymers useful in the hair care compositions of the present invention include all properly defined copolymers of silicone with a non-silicone adhesive polymer. To be useful such copolymers should satisfy the following four criteria:

- 35 (1) when dried the copolymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently attached to the non-silicone portion;
- (3) the molecular weight of the silicone portion is from about 1,000 to about 30,000; and
- 40 (4) the non-silicone portion must render the entire copolymer soluble or dispersible in the hair care composition vehicle and permit the copolymer to deposit on hair. In addition to the graft copolymers described above, useful copolymers include block copolymers containing up to about 50% (preferably from about 10% to about 20%) by weight of one or more polydimethyl siloxane blocks and one or more non-silicone blocks (preferably acrylates or vinyls).

The most preferred polymers comprise a vinyl polymeric backbone, preferably having a  $T_g$  or a  $T_m$   
 45 above about  $-20^\circ\text{C}$  and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that  
 50 this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography.

- 55 Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of



Virginia, 1987, and references cited therein).

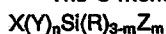
A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface which is entirely covered by silicone even when the concentration of the silicone by weight in the whole polymer is low (2% to 20%). This is demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

Examples of useful copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These copolymers are comprised of monomers A, C and, optionally, B, which are defined as follows. A is at least one free radically polymerizable vinyl monomer or monomers. B, when used, comprises at least one reinforcing monomer copolymerizable with A and is selected from the group consisting of polar monomers and macromers having a T<sub>g</sub> or a T<sub>m</sub> above about -20° C. When used, B may be up to about 98%, preferably up to about 80%, more preferably up to about 20%, of the total monomers in the copolymer. Monomer C comprises from about 0.01% to about 50.0% of the total monomers in the copolymer.

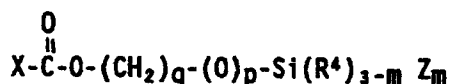
Representative examples of A (hydrophobic) monomers are acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof.

Representative examples of B monomers (hydrophilic) include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization) vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

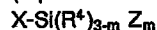
The C monomer has the general formula

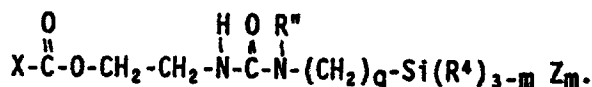
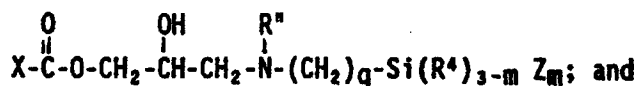
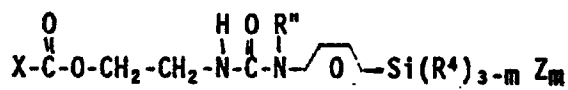
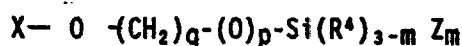


wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions and is pendant from the vinyl polymeric backbone, described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. Preferably, the C monomer has a formula selected from the following group:



(a preferred monomer, particularly preferred when p = 0 and q = 3)

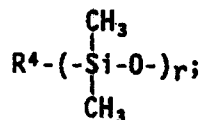




In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; x is



R<sup>1</sup> is hydrogen or -COOH (preferably R<sup>1</sup> is hydrogen); R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH (preferably R<sup>2</sup> is methyl); Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R<sup>4</sup> is alkyl); and r is an integer from about 5 to about 700 (preferably r is about 250).

The polymers of the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of monomer A, from about 0% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99%, most preferably from about 75% to about 95%) of the polymer. The composition of any particular copolymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably have the composition: from about 0% to about 70% (preferably from about 5% to about 70%) monomer A, from about 30% to about 98% (preferably from about 30% to about 80%) monomer B, and from about 1% to about 40% monomer C. Polymers which are dispersible have the preferred composition: from about 0% to about 70% (more preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (more preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% monomer C.

In one aspect of the present invention, the polymers comprise from about 5% to about 98% A monomer, from about 0.01% to about 50% C monomer, and from 0% to about 98% B monomer. In these polymers, it is preferred that A be selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, since such polymers can be dissolved directly in cyclomethicone solvents without requiring co-solvents. This is surprising in view of U.S. Patents 4,693,935 (Mazurek) and 4,728,571 (Clemens et al), which suggest that tertiary alcohols are not suitable A monomers.

Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

- acrylic acid/n-butylmethacrylate/(polydimethylsiloxane (PDMS) macromer-20,000 molecular weight) (10/70/20 w/w/w) (I)
- 5 N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer -20,000 molecular weight) (20/60/20 w/w/w) (II)
- N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/(PDMS macromer - 10,000 molecular weight) (10.5/56/3.5/30 w/w/w/w) (III)
- 10 N,N-dimethylacrylamide/(PDMS macromer - 20,000 molecular wt) (80/20 w/w) (IV)
- t-butylacrylate/t-butyl methacrylate/(PDMS macromer - 10,000 molecular wt) (56/24/20 w/w/w) (V)
- t-butylacrylate/(PDMS macromer-10,000 molecular wt) (80/20 w/w) (IV)
- t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer -10,000 molecular weight) (70/10/20) (VII)
- t-butylacrylate/acrylic acid/(PDMS monomer -10,000 molecular weight) (75/5/20) (VIII)

15 The silicone-containing copolymers described above are synthesized as follows.

The polymers are synthesized by free radical polymerization methods, the general principles of which are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified, as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 10 parts acrylic acid, 70 parts n-butyl-methacrylate, and 20 parts 20K PDMS macromer in a flask. Add sufficient ethyl acetate to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the ethyl acetate by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Maintain temperature at 62°C, with a sufficient rate of argon flow to keep the solution mixed. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

Polymer III: Place 10.5 parts N,N-dimethylmethacrylamide, 56 parts isobutyl methacrylate, 3.5 parts 2-ethylhexylmethacrylate, and 30 parts 10K PDMS macromer in a reaction vessel fitted with an argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene or isopropanol to bring the final monomer concentration to 20% by weight. Begin stirring and sparge with argon for 1 hour. While sparging, heat to 60°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% (if toluene is the solvent) or 0.125% (if isopropanol is the solvent) by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60°C. Allow to react for 6 hours. Terminate the reaction and remove the solvent as with Polymer II.

Carrier

The compositions of the invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, most preferably from about 10.0% to about 90.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate solvent will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on hair (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone copolymer being used. The nature and proportion of B monomer in the copolymer largely determines its polarity and solubility characteristics. The silicone copolymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (such as ethanol, isopropanol), hydro-alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicon derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other.

Where the hair care compositions are conditioner compositions, the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following three concurrently-filed patent applications: Vehicle Systems for Use in Hair Care Compositions, Bolich, Norton and Russell, docket numbers 4000, 4001 and 4002, incorporated herein by reference.

Other carriers, suitable for use with the present invention are, for example, those used in the formulation

of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also require an emulsifying agent to keep the silicone copolymer  
 5 homogeneously dispersed in solution. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is present at a level of from about 0.25% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

10

### Optional Ingredients

15 The hair care compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

20

#### Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly, shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably  
 25 from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and  
 30 alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl  
 35 and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with about 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

40 Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.  
 45 Such a mixture also comprises from about 0 to about 20% by weight  $\text{C}_{12-13}$  compounds; from about 60 to about 100% by weight of  $\text{C}_{14-15-16}$  compounds, from about 0 to about 20% by weight of  $\text{C}_{17-18-19}$  compounds; from about 3 to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to about 90% by weight of compounds having a degree of ethoxylation of from about 1 to about 4; from about 10 to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to  
 50 about 8; and from about 0.1 to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



55 wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having about 8 to about 24 carbon atoms.

preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $\text{C}_{12-18}$  n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

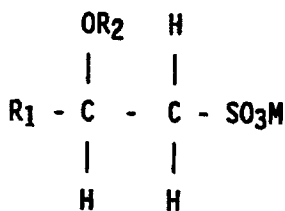
Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of  $\alpha$ -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $\text{SO}_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous  $\text{SO}_2$ , etc., when used in the gaseous form.

The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific  $\alpha$ -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, Pflaumer and Kessler, issued July 25, 1967, incorporated herein by reference.

Another class of anionic organic surfactants are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



where  $\text{R}_1$  is a straight chain alkyl group having from about 6 to about 20 carbon atoms,  $\text{R}_2$  is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Specific examples of  $\beta$ -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- $\beta$ -methoxydecanesulfonate, sodium 2-methoxy-tridecanesulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecyl-sulfonate, sodium  $\beta$ -methoxyoctadecylsulfonate, and ammonium  $\beta$ -n-propoxydodecylsulfonate.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

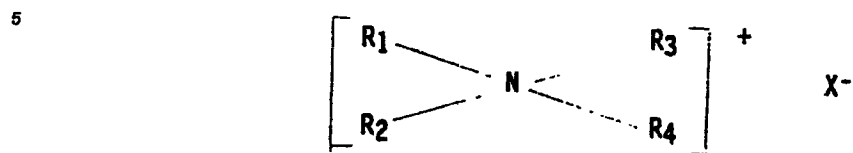
Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl

aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.
  2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.
  3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.
  4. Long chain tertiary amine oxides corresponding to the following general formula:
 
$$R_1R_2R_3N \longrightarrow O$$
 wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxy propyl)amine oxide, dimethylhexadecylamine oxide.
  5. Long chain tertiary phosphine oxides corresponding to the following general formula:
 
$$RR'R''P \longrightarrow O$$
 wherein  $R$  contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecyldimethyl phosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)-phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.
  6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.
- Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's. *Detergents & Emulsifiers*, (North American edition 1979); Schwartz, et al., *Surface Active Agents, Their Chemistry and Technology*, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from

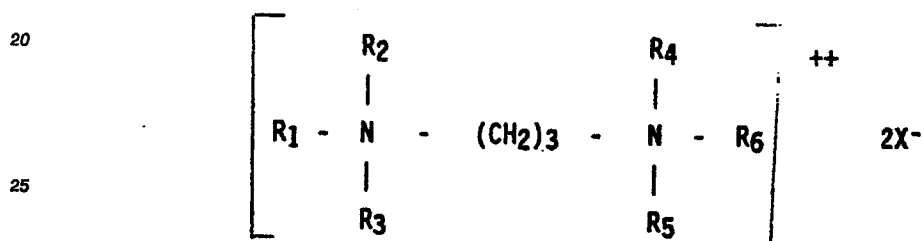
about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein  $R_1$ - $R_4$  are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and  $X$  is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

Other quaternary ammonium salts useful herein have the formula:



wherein  $R_1$  is an aliphatic group having from about 16 to about 22 carbon atoms,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and  $X$  is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

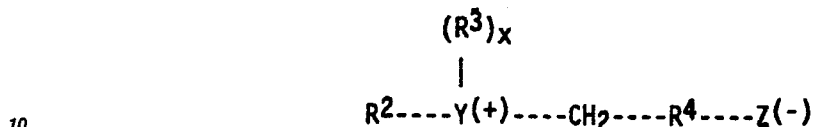
Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein  $R_1$  and  $R_2$  have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, diéicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can



be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety;  $Y$  is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms;  $X$  is 1 when  $Y$  is a sulfur atom, and 2 when  $Y$  is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and  $Z$  is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

- 4-[N-N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecylphosphonio]-2-hydroxy-propane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gammacarboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the  $RCONH(CH_2)_3$  radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof are preferred for use herein.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as

cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions should be between about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

#### Method of Use

The hair care compositions of the present invention are used in conventional ways to provide the hair conditioning/styling/hold benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, and tonic products). By "effective amount" is meant an amount sufficient to provide the hair conditioning/styling/hold benefits desired considering the length and texture of the hair, and the type of product used. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to the hair, the hair is dried and styled in the usual ways of the user.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

The following table defines the silicone copolymers used in the examples (weight ratios given refer to proportion added to reaction mix):

- |    |   |
|----|---|
| 35 | Copolymer #1 10/70/20 acrylic acid/n-butylmethacrylate/silicone macromer S2, polymer molecular weight about 100,000                                     |
|    | Copolymer #2 10/70/20 dimethylacrylamide/isobutyl methacrylate/silicone macromer S2, polymer molecular weight about 400,000                             |
|    | Copolymer #3 60/20/20 diallyldimethyl ammonium chloride/isobutyl methacrylate/silicone macromer S1, polymer molecular weight about 500,000              |
| 40 | Copolymer #4 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, polymer molecular weight about 400,000                                     |
|    | Copolymer #5 10/70/20 acrylic acid/n-butyl methacrylate/silicone macromer S1, polymer molecular weight about 300,000                                    |
| 45 | Copolymer #6 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000                                  |
|    | Copolymer #7 60/25/15 N,N-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000                     |
|    | Copolymer #8 12/64/4/20 N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000 |
| 50 | Copolymer #9 30/40/10/20 dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000    |
|    | Copolymer #10 80/20 t-butylacrylate/PDMS macromer S2, polymer molecular weight about 150,000  |

Silicone macromer S1- has a molecular weight of about 20,000 and is prepared in a manner similar to Example C-2c of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

Silicone macromer S2- has a molecular weight of about 10,000 and is prepared in a manner similar to Example C-2b of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

EXAMPLE 1

The following is a hair spray composition representative of the present invention.

Component	Weight %
Silicone Copolymer #4	2.00
Ethanol	72.90
Perfume	0.10
Isobutane propellant	25.00

This product is prepared by adding the silicone copolymer and perfume to the ethanol and mixing for several hours until all the polymer is dissolved. This "concentrate" is then placed in aerosol cans which are fitted with valves crimped under vacuum and then filled through the valve stem with isobutane dispensed by a pressure filler.

EXAMPLE II

The following is a shampoo composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #2	1.00
Chloropropyl heptamethyl cyclotetrasiloxane	3.00
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs. fluid	0.50
<u>Main Mix</u>	
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan gum	1.20
Kathon CG <sup>1</sup>	0.04
Citric acid to pH 4.5	q.s.
Double reverse osmosis (DRO) H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Rohm & Haas

The Styling Agent and Premix are blended separately in a conventional manner. The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150° F with agitation for 1/2 hour. The Styling Agent and Premix are then added sequentially with about ten minutes agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

EXAMPLE III

The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	7.00
Cocamide MEA	2.50
Silicone Copolymer #3	1.00
Natrosol 250H <sup>1</sup>	1.00
Glydant <sup>2</sup>	0.37
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>2</sup> preservative commercially available from Glyco, Inc.

The shampoo is made by first dispersing the Natrosol and silicone copolymer in the water for about 1 hour with conventional agitation. The remaining ingredients are then added.

#### EXAMPLE IV

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent Premix</u>	
Silicone Copolymer #8	2.00
Phenethylpentamethyl disiloxane	6.00
Octamethyl cyclotetrasiloxane	3.00
<u>Xanthan Premix</u>	
Xanthan gum	0.25
DRO H <sub>2</sub> O	25.00
<u>Main Mix</u>	
Dihydrogenated tallow-dimethylammonium chloride (DTDMAC)	0.50
EDTA, disodium salt	0.10
D.C. 929 <sup>1</sup>	2.00
Perfume	0.10
Poly Surf C <sup>2</sup>	0.75
Locust bean gum	0.75
Kathon CG <sup>3</sup>	0.04
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> amodimethicone, commercially available from Dow Corning

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Rohm and Haas

The Styling Agent and Xanthan Premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating with agitation to 95° C for about 1/2 hour. As the batch is cooled, the Styling Agent and Xanthan Premixes are added at about 60° C with vigorous mixing. The batch is then cooled to ambient temperature.

EXAMPLE V

The following is a styling rinse composition representative of the present invention.

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Component	Weight %
<u>Premix A</u>	
Silicone Copolymer #3	2.00
DRO H <sub>2</sub> O	10.00
<u>Premix B</u>	
Silicone Copolymer #4	2.00
DRO H <sub>2</sub> O	15.00
NaOH solution (50%)	0.20
<u>Main Mix</u>	
Poly Surf C <sup>1</sup>	1.00
Stearamide DEA	0.50
Ethanol	10.00
Perfume	0.20
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

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Both premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating to about 60° C with mixing. The premixes are then added to the Main Mix with agitation for about 1/2 hour and the batch is cooled to ambient temperature. Either sodium hydroxide or citric acid, if necessary, is added to adjust composition to pH 6.5.

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EXAMPLE VI

The following is a hair grooming tonic composition representative of the present invention.

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Component	Weight %
Silicone Copolymer #9	0.70
Perfume	0.10
Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

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EXAMPLE VII

The following is a shampoo composition representative of the present invention.

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Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Silicone Copolymer #6	2.00
Ethanol	10.00
PEG 150 distearate	2.00
Glydant <sup>1</sup>	0.38
Perfume	1.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70° C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. Composition pH is adjusted to 6.3 by the addition of citric acid or sodium hydroxide, if necessary.

#### EXAMPLE VIII

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #5	3.00
Phenylpentamethyl disiloxane	9.00
<u>Premix</u>	
Silicone gum GE SE76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf C <sup>2</sup>	0.60
Locust bean gum	0.50
EDTA, disodium salt	0.15
DTDMAC	0.65
Glydant <sup>3</sup>	0.40
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Glyco, Inc.

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95° C for 1/2 hour with agitation. As the batch is cooled to about 60° C, the Premix and Styling Agent mix are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE IX

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #10	3.00
Octamethyl cyclotetrasiloxane	9.00
<u>Premix</u>	
Silicone gum GE SE 76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf C <sup>2</sup>	1.25
Stearamide DEA	0.40
DTDMAC	0.50
Kathon CG <sup>3</sup>	0.03
Imidazole	0.15
Perfume	0.10
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Rohm & Haas

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95 °C for 1/2 hour with agitation. As the batch is cooled to about 60 °C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE X

The following is a cold-wave hair perm composition representative of the present invention.

Component	Weight %
Thioglycolic acid	5.00
Monoethanolamine	6.00
Silicone Copolymer #3	1.50
PEG 10 monostearate	0.50
DRO H <sub>2</sub> O	q.s.

The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60 °C and then cooling to ambient temperature.

#### EXAMPLE XI

The following is a hair conditioner composition representative of the present invention.

Component	Weight %
<u>Styling Agent Premix</u>	
Silicone Copolymer #9	1.00
Phenyl pentamethyl disiloxane	4.00
<u>Silicone Premix</u>	
Silicone gum, GE SE76 <sup>1</sup>	0.30
Octamethyl cyclotetrasiloxane	1.70
<u>Main Mix</u>	
Cetyl alcohol	1.00
Quaternium 18 <sup>2</sup>	0.85
Stearyl alcohol	0.70
Natrosol 250 MBR <sup>3</sup>	0.50
Ceteareth-20	0.35
Fragrance	0.20
Dimethicone copolyol	0.20
Citric acid	0.13
Methylchlorisothiazolinone, methylisothiazolinone	0.04
Sodium chloride	0.01
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> Ditalow quaternary ammonium compound, commercially available from Sherex

<sup>3</sup> hydroxyethyl cellulose material, commercially available from Aquaion Co.

The product is prepared by comixing all the Main Mix ingredients, heating to about 60 °C with mixing, and colloid milling down to about 45 °C. At this temperature, the two premixes are added separately with moderate agitation and the batch allowed to cool to ambient temperature.

#### EXAMPLE XII

The following is a styling gel composition representative of the present invention.

Component	Weight %
Silicone Copolymer #7	2.00
Carbopol 940 <sup>1</sup>	0.75
Triethanolamine	1.00
Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> cross-linked polyacrylic acid, commercially available from B. F. Goodrich

This batch is made by mixing the listed components together in a conventional manner.

#### EXAMPLE XIII



The following is a hair mousse composition representative of the present invention.

Component	Weight %
Silicone Copolymer #7	3.00
Ethanol	15.00
Cocamine oxide	0.60
D.C. 190 <sup>1</sup>	0.20
Cocamide DEA	0.30
Perfume	0.10
Isobutane	7.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> dimethicone copolyol, commercially available from Dow Corning

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

#### EXAMPLE XIV

The following is a pump hair spray composition representative of the present invention.

Component	Weight %
Silicone Copolymer #1	2.50
Dibutyl phthalate	0.20
Phenyldimethicone	0.30
Perfume	0.05
Aminomethyl propanol	0.20
Ethanol	q.s.

This composition is made by mixing the listed components together in a conventional manner.

When the compositions defined in Examples I-XIV are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

#### Claims

1. A hair care composition characterized in that it comprises:

(a) from 0.1% to 10.0% of a 'copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising C monomers and components selected from A monomers, B monomers, and mixtures thereof, wherein:

A is at least one free radically polymerizable vinyl monomer, preferably selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, the amount by weight of A monomer, when used, being up to about 98% by weight of the total weight of all monomers in said copolymer;

B is at least one reinforcing monomer copolymerizable with A, the amount by weight of B monomer, when used, being up to about 98% of the total weight of all monomers in said copolymer, said B monomer being selected from polar monomers and macromers; and

C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula

$X(Y)_nSi(R)_{3-m}(Z)_m$  wherein

X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization

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n is 0 or 1

m is an integer from 1 to 3

wherein C comprises from 0.01% to 50% of the copolymer; and

(b) from 0.5% to 99.5% of a carrier suitable for application to hair.

10 2. A hair care composition according to Claim 1 characterized in that the copolymer comprises from 5% to 98% A monomer, from 0.01% to 50% C monomer and from 0% to 98% B monomer.

3. A hair care composition according to Claim 1 characterized in that the copolymer comprises from 0% to 98% A monomer, from 0.01% to 50% C monomer, and from 7.5% to 80% B monomer.

4. A hair care composition characterized in that it comprises:

15 (a) from 0.1% to 10.0% of a silicone-containing copolymer containing a silicone portion having a molecular weight of from 1,000 to 50,000 which is covalently attached to a non-silicone portion; and

(b) from 0.5% to 99.5% of a carrier suitable for application to hair;

the copolymer and carrier selected such that, when dried, the copolymer phase separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-

20 silicone portion.

5. A hair care composition characterized in that it comprises:

(a) from 0.1% to 10.0% of a silicone-containing copolymer having a vinyl polymeric backbone and having grafted to the backbone a polydimethylsiloxane macromer having a weight average molecular weight between 1,000 and 50,000; and

25 (b) from 0.5% to 99.5% of a carrier suitable for application to hair;

the polymer and carrier selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.

6. A hair care composition according to any of Claims 1-5 characterized in that it is in the form of a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, preferably selected from

30 alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.

7. A hair care composition according to any of Claims 1-5 characterized in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 10.0% of a lipid vehicle material, preferably

35 selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and from 0.05% to 5.0% of a cationic surfactant, preferably a quaternary ammonium surfactant.

8. A hair care composition according to any of Claims 1-5 characterized in that it is in a form selected from hair sprays, mousses, hair tonics, and gels.

9. A method of conditioning and styling hair characterized in that it comprises applying to the hair an effective amount of the composition according to any of Claims 1-8.

40 10. A copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising from 0.01% to 50% C monomers, from 5% to 98% A monomers, and from 0% to 98% B monomers, wherein:

A is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof;

45 B is at least one reinforcing monomer copolymerizable with A selected from polar monomers and macromers, and is preferably selected from acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof; and

C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula

$X(Y)_nSi(R)_{3-m}(Z)_m$  wherein

X is a vinyl group copolymerizable with the A and B monomers

50 Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization

55 n is 0 or 1, and

m is an integer from 1 to 3.

11. Copolymers according to Claim 10 characterized in that they are selected from t-butylacrylate/t-butylmethacrylate/(PDMS macromer - 10,000 molecular wt) 56/24/20

t-butylacrylate/(PDMS macromer - 10,000 molecular wt.) 80/20  
t-butylacrylate/acrylic acid/(PDMS macromer-10,000 molecular wt.) 75/5/20, and mixtures thereof; which are preferably dissolved in a cyclomethicone solvent.'

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54 Hair conditioning and styling compositions.

57 Hair care compositions which provide improved styling and hair conditioning properties are disclosed. These compositions comprise from about 0.1% to about 10.0% of a specifically-defined silicone copolymer and from about 0.5% to about 99.5% of a carrier suitable for application to hair.

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## HAIR CONDITIONING AND STYLING COMPOSITIONS

TECHNICAL FIELD

This application is a continuation-in-part of U.S. Application Serial No. 390,559, Torgerson, Bollich and Garbe, filed August 7, 1989.

The present invention relates to hair care compositions which have improved hair conditioning and style retention properties while still leaving the hair with a natural non-sticky feel. These compositions utilize a group of specific silicone macromer-containing copolymers.

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has now been discovered that hair care compositions comprising certain specifically-defined silicone macromer-containing copolymers provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays, tonics, lotions, gels, and mousses. The compositions provide these benefits to hair without leaving the hair with a stiff or sticky/tacky feel and without negatively affecting dry hair properties, such as ease of combing. Further, hair to which the compositions of the present invention have been applied may be restyled several times without requiring reapplication of the compositions.

These results are surprising since other materials which have been typically used in hair care compositions to provide style retention, such as resins and gums, generally hurt dry hair properties (e.g., combing) and leave hair with a sticky and/or stiff feel. Furthermore, silicone materials typically used for hair conditioning tend to hurt style retention.

Siloxanes (see, for example, U.S. Patent 3,208,911, Oppliger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. U.S. Patent 4,601,902, Fridt et al., issued July 22, 1986, describes hair conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. U.S. Patent 4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. U.S. Patent 4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include siloxane components containing substituents to provide attachment to hair. Japanese Published Application 56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxane-oxyalkylene copolymer together with an acrylic resin. U.S. Patent 4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes). Polyether-modified polysiloxanes are also disclosed for use in shampoos in U.S. Patent 3,957,970, Korkis, issued May 18, 1976. U.S. Patent 4,185,087, Morlino, issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties.

Siloxane-derived materials have also been used in hair styling compositions. Japanese Published Application 56-092,811, Lion Corporation, published December 27, 1979, describes hair setting composi-

tions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. U.S. Patent 4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which include polydiorganosiloxanes and a cationic organic polymer are taught in U.S. Patent 4,733,677, Gee et al., issued March 29, 1988, and U.S. Patent 4,724,851, Cornwall et al., issued February 16, 1988. Finally, European Patent Application 117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid.

Siloxane-containing polymers have also been used in non-hair care applications. U.S. Patent 4,136,250, Mueller et al., issued January 23, 1979, relates to polymeric materials used in biological contexts where oxygen permeable and tissue compatible membranes are required. They can also be used as carriers for biologically-active substances. These materials are hydrophilic water-insoluble gels which include a low molecular weight terminal olefinic siloxane macromer and a polymer containing water-soluble monoolefinic monomer. U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, describes pressure sensitive adhesive compositions which include a copolymer with a vinyl polymeric backbone having grafted thereto polysiloxane moieties. U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, relates to adhesive release coating compositions which comprise polysiloxane-grafted copolymers and blends of those copolymers with other polymeric materials. None of these last three patents suggest the use of the disclosed siloxane-containing polymers in hair care compositions.

It is an object of the present invention to formulate hair care compositions which provide effective hair conditioning and style retention properties.

It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention from a single composition.

It is a further object of the present invention to formulate hair care compositions which provide good style retention without leaving hair with a stiff or sticky/tacky feel.

It is a further object of the present invention to provide an improved method for styling and conditioning hair.

These and other objects will become readily apparent from the detailed description which follows.

Unless otherwise indicated, all percentages and ratios herein are by weight.

## SUMMARY OF THE INVENTION

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The present invention relates to hair care compositions comprising

(a) from about 0.1% to about 10.0% of a silicone-containing copolymer having a vinyl polymeric backbone, preferably having a T<sub>g</sub> above about -20°C, and having grafted to the backbone a polydimethylsiloxane macromer having a weight average molecular weight between about 1,000 and about 50,000; and

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(b) from about 0.5% to about 99.5% of a carrier suitable for application to hair;

the polymer and carrier are selected such that, when dried, the polymer phase-separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. Preferred silicone-containing copolymers are those having a molecular weight of from about 10,000 to about 1,000,000 and comprising C monomers and components selected from A monomers, B monomers, and mixtures thereof, wherein A is a lipophilic, low polarity free radically polymerizable vinyl monomer, such as methacrylic or acrylic esters; B comprises a hydrophilic polar monomer which is copolymerizable with A, such as acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, vinyl pyrrolidone, or quaternized dimethylaminoethylmethacrylate; and C is a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, based on polydimethylsiloxane. These polymers contain from about 0.1% to about 50.0% of C macromer and from about 50.0% to about 99.9% of the combination of A and B monomers.

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## DETAILED DESCRIPTION OF THE INVENTION

The essential, as well as the optional, components of the present invention are described below.

Silicone-Containing Copolymer

The compositions of the present invention contain from about 0.1% to about 10.0%, preferably from about 0.5% to about 8.0%, of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers should have a weight average molecular weight of from about 10,000 to about 1,000,000 (preferably from about 30,000 to about 300,000) and, preferably, have a Tg of at least about -20° C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone; and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

In its broadest sense, the polymers useful in the hair care compositions of the present invention include all properly defined copolymers of silicone with a non-silicone adhesive polymer. To be useful such copolymers should satisfy the following four criteria:

- (1) when dried the copolymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently attached to the non-silicone portion;
- (3) the molecular weight of the silicone portion is from about 1,000 to about 50,000; and
- (4) the non-silicone portion must render the entire copolymer soluble or dispersible in the hair care composition vehicle and permit the copolymer to deposit on hair. In addition to the graft copolymers described above, useful copolymers include block copolymers containing up to about 50% (preferably from about 10% to about 20%) by weight of one or more polydimethyl siloxane blocks and one or more non-silicone blocks (preferably acrylates or vinyls).

Preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg above about -20° C and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron microscopy. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface which is entirely covered by silicone even when the concentration of the silicone by weight in the whole polymer is low (2% to 20%). This is demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

In its broadest aspect, the copolymers utilized in the present application comprise C monomers together with monomers selected from the group consisting of A monomers, B monomers, and mixtures thereof. These copolymers contain at least A or B monomers, together with C monomers, and preferred copolymers contain A, B and C monomers.

Examples of useful copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These copolymers are comprised of monomers A, C and, optionally, B, which are defined as follows. A is at least one free radically polymerizable vinyl monomer or monomers. B, when used, comprises at least one reinforcing monomer copolymerizable with A and is selected from the group consisting of polar monomers and macromers

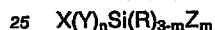


having a Tg or a Tm above about -20° C. When used, B may be up to about 98%, preferably up to about 80%, more preferably up to about 20%, of the total monomers in the copolymer. Monomer C comprises from about 0.01% to about 50.0% and the total monomers in the copolymer.

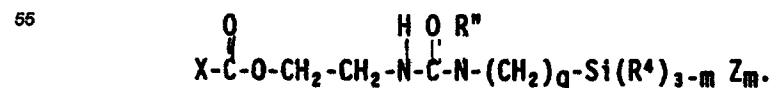
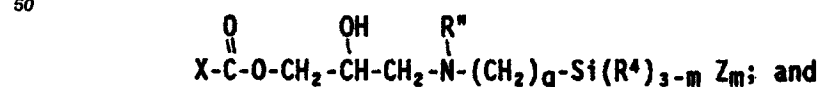
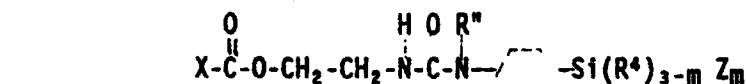
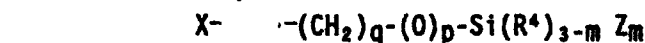
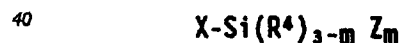
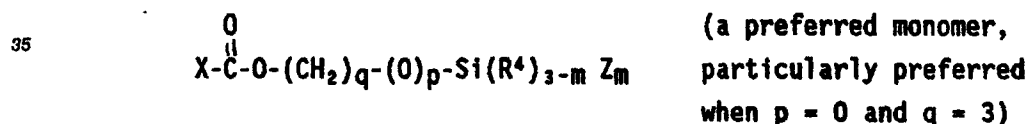
Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Representative examples of B (hydrophilic) monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butylacrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization) vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

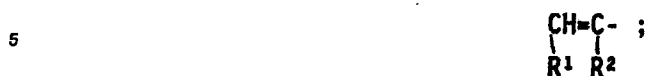
The C monomer has the general formula



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions and is pendant from the vinyl polymeric backbone, described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. Preferably, the C monomer has a formula selected from the following group:



In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is



R<sup>1</sup> is hydrogen or -COOH (preferably R<sup>1</sup> is hydrogen); R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH (preferably R<sup>2</sup> is methyl); Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R<sup>4</sup> is alkyl); and r is an integer from about 5 to about 700 (preferably r is about 250).

The polymers of the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of monomer A, from about 0% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99%, most preferably from about 75% to about 95%) of the polymer. The composition of any particular copolymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably have the composition: from about 0% to about 70% (preferably from about 5% to about 70% monomer A, from about 30% to about 98% (preferably from about 30% to about 80% monomer B, and from about 1% to about 40% monomer C. Polymers which are dispersible have the preferred composition: from about 0% to about 70% (more preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (more preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% monomer C.

In one aspect of the present invention, the polymers comprise from about 5% to about 98% A monomer, from about 0.01% to about 50% C monomer, and from 0% to about 98% B monomer. In these polymers, it is preferred that A be selected from t-butylacrylate, t-butylmethacrylate, and mixtures thereof, since such polymers can be dissolved directly in cyclomethicone solvents without requiring co-solvents. This is surprising in view of U.S. Patents 4,693,935 (Mazurek) and 4,728,571 (Clemens et al.) which suggest that tertiary alcohols are not suitable A monomers.

Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

acrylic acid/n-butylmethacrylate/(polydimethylsiloxane (PDMS) macromer-20,000 molecular weight) (10/70/20 w/w/w) (I)

N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer -20,000 molecular weight) (20/60/20 w/w/w) (II)

dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexylmethacrylate/(PDMS macromer-20,000 molecular weight) (25/40/15/20 w/w/w/w) (III)

dimethylacrylamide/(PDMS macromer - 20,000 molecular weight) (80/20 w/w) (IV)

t-butylacrylate/t-butylmethacrylate/(PDMS macromer - 10,000 molecular weight) (56/24/20 w/w/w) (V)

t-butylacrylate/(PDMS macromer - 10,000 molecular weight) (80/20 w/w) (VI)

t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer -10,000 molecular weight) (70/10/20) (VII)

t-butylacrylate/acrylic acid/(PDMS macromer - 10,000 molecular weight) (75/5/20) (VIII)

The silicone-containing copolymers described above are synthesized as follows.

The polymers are synthesized by free radical polymerization methods, the general principles of which are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. Iisher, date, pages). The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is

reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc.). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 10 parts acrylic acid, 70 parts n-butylmethacrylate, and 20 parts 20K PDMS macromer in a flask. Add sufficient ethyl acetate to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60 °C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the ethyl acetate by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62 °C, with a sufficient rate of argon flow to keep the solution mixed. Add initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

Polymer III: Place 25 parts dimethylaminoethylmethacrylate, 15 parts 2-ethylhexylmethacrylate, 40 parts isobutylmethacrylate, and 20 parts 20K PDMS macromer in a reaction vessel fitted with a mechanical stirrer, argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene to bring the final monomer concentration to 30% by weight. Begin stirring and sparge with argon for 2 hours. While sparging, heat to 60 °C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.15% by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60 °C. Allow to react for 24 hours. Terminate the reaction and remove the solvent as with Polymer I.

#### Carrier

The compositions of the invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, most preferably from about 10.0% to about 90.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate carrier will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on hair (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone copolymer being used. The nature and proportion of B monomer in the copolymer largely determines its polarity and solubility characteristics. The silicone copolymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (such as ethanol, isopropanol), hydro-alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane,

octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicon derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other.

Where the hair care compositions are conditioner compositions, the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, 3rd edition, D. Swern, ed., 1979, incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.5% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following three concurrently-filed patent applications: Vehicle System for Use in Hair Care Compositions, Bolich, Norton and Russell, Docket numbers 4000, 4001, and 4002, incorporated herein by reference.

Other carriers, suitable for use with the present invention are, for example, those used in the formulation of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also require an emulsifying agent to keep the silicone copolymer homogeneously dispersed in solution. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is present at a level of from about 0.25% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

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#### Optional Ingredients

The hair care compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

## Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with about 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to about 20% by weight  $\text{C}_{12-13}$  compounds; from about 60 to about 100% by weight of  $\text{C}_{14-15-16}$  compounds, from about 0 to about 20% by weight of  $\text{C}_{17-18-19}$  compounds; from about 3 to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to about 90% by weight of compounds having a degree of ethoxylation of from about 1 to about 4; from about 10 to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1 to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $\text{C}_{12-18}$  n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of  $\alpha$ -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $\text{SO}_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous  $\text{SO}_2$ , etc., when used in the

gaseous form.

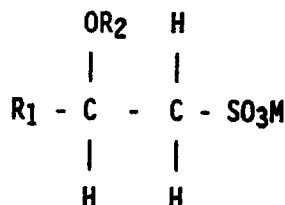
The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific  $\alpha$ -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, Pflaumer and Kessler, issued July 25, 1967, incorporated herein by reference.

Another class of anionic organic surfactants are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:

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where  $\text{R}_1$  is a straight chain alkyl group having from about 6 to about 20 carbon atoms,  $\text{R}_2$  is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Specific examples of  $\beta$ -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- $\beta$ -methoxydecane-sulfonate, sodium 2-methoxy-tridecane-sulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecylsulfonate, sodium  $\beta$ -methoxyoctadecylsulfonate, and ammonium  $\beta$ -n-propoxydodecylsulfonate.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's. Detergents and Emulsifiers 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

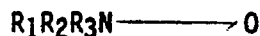
Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyldodecylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:

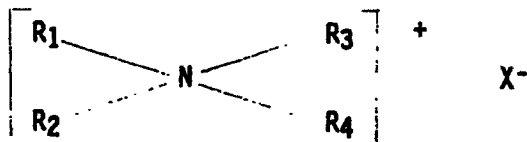


wherein  $R$  contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

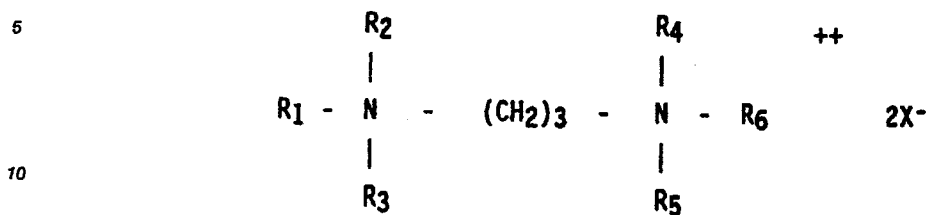
Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein  $R_1$ - $R_4$  are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and  $X$  is an anion selected from halogen, acetate, phosphate, nitrate and

alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

Other quaternary ammonium salts useful herein have the formula:

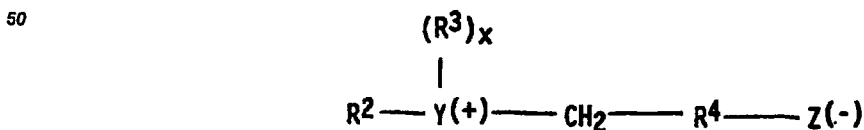


wherein  $R_1$  is an aliphatic group having from about 16 to about 22 carbon atoms,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and  $X$  is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein  $R_1$  and  $R_2$  have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety;  $Y$  is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group



containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R<sup>4</sup> is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

5 Examples of such surfactants include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-5-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecylphosphonio]-2-hydroxy-propane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 10 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(i-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 15 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, 20 oleyl dimethyl gammacarboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alphacarboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the RCONH(CH<sub>2</sub>)<sub>3</sub> radical is attached to the nitrogen atom of the betaine are also useful in this invention.

25 Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are 30 sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

35 The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, ethoxylated alkyl sulfates and mixtures thereof are preferred for use herein.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, 40 e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonooethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as 45 citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin and propylene glycol. Such optional ingredients generally are used individually at levels of from 50 about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions should be between about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

55 The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

Method of Use

The hair care compositions of the present invention are used in conventional ways to provide the hair conditioning/styling/hold benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, and tonic products). By "effective amount" is meant an amount sufficient to provide the hair conditioning/styling/hold benefits desired considering the length and texture of the hair, and the type of product used. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to the hair, the hair is dried and styled in the usual ways of the user.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

The following table defines the silicone copolymers used in the examples (weight ratios given refer to proportion added to reaction mix):

- Copolymer #1 10/70/20 acrylic acid/n-butylmethacrylate/silicone macromer S2, polymer molecular weight about 100,000
- Copolymer #2 10/70/20 dimethylaminoethyl methacrylate/isobutyl methacrylate/silicone macromer S2, polymer molecular weight about 400,000
- Copolymer #3 60/20/20 quaternized dimethylaminoethyl methacrylate/isobutyl methacrylate/silicone macromer S1, polymer molecular weight about 500,000
- Copolymer #4 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, polymer molecular weight about 400,000
- Copolymer #5 10/70/20 acrylic acid/n-butyl methacrylate/silicone macromer S1, polymer molecular weight about 300,000
- Copolymer #6 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000
- Copolymer #7 60/25/15 N,N-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000
- Copolymer #8 12/64/4/20 N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
- Copolymer #9 30/40/10/20 dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
- Copolymer #10 80/20 t-butylacrylate/PDMS macromer S2, polymer molecular weight about 150,000

Silicone macromer S1- has a molecular weight of about 20,000 and is prepared in a manner similar to Example C-2c of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

Silicone macromer S2- has a molecular weight of about 10,000 and is prepared in a manner similar to Example C-2b of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

EXAMPLE 1

The following is a hair spray composition representative of the present invention

Component	Weight %
Silicone Copolymer #4	2.00
Ethanol	72.90
Perfume	0.10
Isobutane propellant	25.00

This product is prepared by adding the silicone copolymer and perfume to the ethanol and mixing for

several hours until all the polymer is dissolved. This "concentrate" is then placed in aerosol cans which are fitted with valves crimped under vacuum and then filled through the valve stem with isobutane dispensed by a pressure filler.

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EXAMPLE II

The following is a shampoo composition representative of the present invention.

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Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #2	1.00
Chlorpropyl heptamethyl cyclotetrasiloxane	3.00
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs. fluid	0.50
<u>Main Mix</u>	
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan gum	1.20
Kathon CG <sup>1</sup>	0.04
Citric acid to pH 4.5	q.s.
Double reverse osmosis (DRO) H <sub>2</sub> O	q.s.

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<sup>1</sup> preservative commercially available from Rohm & Haas

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The Styling Agent and Premix are blended separately in a conventional manner. The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150° F with agitation for 1/2 hour. The Styling Agent and Premix are then added sequentially with about ten minutes agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

EXAMPLE III

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The following is a shampoo composition representative of the present invention.

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Component	Weight %
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	7.00
Cocamide MEA	2.50
Silicone Copolymer #3	1.00
Natrosol 250H <sup>1</sup>	1.00
Glydant <sup>2</sup>	0.37
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>2</sup> preservative commercially available from Glyco, Inc.

The shampoo is made by first dispersing the Matrosol and silicone copolymer in the water for about 1 hour with conventional agitation. The remaining ingredients are then added.

#### EXAMPLE IV

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent Premix</u>	
Silicone Copolymer #8	2.00
Phenethylpentamethyl disiloxane	6.00
Octamethyl cyclotetrasiloxane	3.00
<u>Xanthan Premix</u>	
Xanthan gum	0.25
DRO H <sub>2</sub> O	25.00
<u>Main Mix</u>	
Dihydrogenated tallow-dimethylammonium chloride (DTDMAC)	0.50
EDTA, disodium salt	0.10
D.C. 929 <sup>1</sup>	2.00
Perfume	0.10
Poly Surf C <sup>2</sup>	0.75
Locust bean gum	0.75
Kathon CG <sup>3</sup>	0.04
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> amodimethicone, commercially available from Dow Corning

<sup>2</sup> hydrophobically- modified hydroxyethyl cellulose, commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Rohm and Haas

The Styling Agent and Xanthan Premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating with agitation to 95° C for about 1/2 hour. As the batch is cooled, the Styling Agent and Xanthan Premixes are added at about 60° C with vigorous mixing. The batch is then cooled to ambient temperature.

#### EXAMPLE V

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Premix A</u>	
Silicone Copolymer #3	2.00
DRO H <sub>2</sub> O	10.00
<u>Premix B</u>	
Silicone Copolymer #4	2.00
DRO H <sub>2</sub> O	15.00
NaOH solution (50%)	0.20
<u>Main Mix</u>	
Poly Surf C <sup>1</sup>	1.00
Stearamide DEA	0.50
Ethanol	10.00
Perfume	0.20
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

Both premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating to about 60° C with mixing. The premixes are then added to the Main Mix with agitation for about 1/2 hour and the batch is cooled to ambient temperature. Either sodium hydroxide or citric acid, if necessary, is added to adjust composition pH to 6.5.

#### EXAMPLE VI

The following is a hair grooming tonic composition representative of the present invention.

Component	Weight %
Silicone Copolymer #9	0.70
Perfume	0.10
Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

#### EXAMPLE VII

The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Silicone Copolymer #6	2.00
Ethanol	10.00
PEG 150 distearate	2.00
Glydant <sup>1</sup>	0.38
Perfume	1.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70 °C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. Composition pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

#### EXAMPLE VIII

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #5	3.00
Phenylpentamethyl disiloxane	9.00
<u>Premix</u>	
Silicone Gum GE SE76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf C <sup>2</sup>	0.60
Locust bean gum	0.50
EDTA, disodium salt	0.15
DTDMAC	0.65
Glydant <sup>3</sup>	0.40
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Glyco, Inc.

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95 °C for 1/2 hour with agitation. As the batch is cooled to about 60 °C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE IX

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #10	3.00
Octamethyl cyclotetrasiloxane	9.00
<u>Premix</u>	
Silicone Gum GE SE76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf C <sup>2</sup>	1.25
Stearamide DEA	0.40
DTDMAC	0.50
Kathon CG <sup>3</sup>	0.03
Imiazole	0.15
Perfume	0.10
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Rohm & Haas

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95° C for 1/2 hour with agitation. As the batch is cooled to about 60° C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE X

The following is a cold-wave hair perm composition representative of the present invention.

Component	Weight %
Thioglycolic acid	5.00
Monoethanolamine	6.00
Silicone Copolymer #3	1.50
PEG 10 monostearate	0.50
DRO H <sub>2</sub> O	q.s.

The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60° C and then cooling to ambient temperature.

#### EXAMPLE XI

The following is a hair conditioner composition representative of the present invention.

Component	Weight %
<u>Styling Agent Premix</u>	
Silicone Copolymer #9	1.00
Phenyl pentamethyl disiloxane	4.00
<u>Silicone Premix</u>	
Silicone gum, GE SE76 <sup>1</sup>	0.30
Octamethyl cyclotetrasiloxane	1.70
<u>Main Mix</u>	
Cetyl alcohol	1.00
Quaternium 18 <sup>2</sup>	0.85
Stearyl alcohol	0.70
Natrosol 250 MBR <sup>3</sup>	0.50
Ceteareth-20	0.35
Fragrance	0.20
Dimethicone copolyol	0.20
Citric acid	0.13
Methylchloroisothiazolinone, methylisothiazolinone	0.04
Sodium chloride	0.01
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> Ditalow quaternary ammonium compound, commercially available from Sherex

<sup>3</sup> hydroxyethyl cellulose material, commercially available from Aqualon Co.

The product is prepared by combining all the Main Mix ingredients, heating to about 60° C with mixing, and colloid milling down to about 45° C. At this temperature, the two premixes are added separately with moderate agitation and the batch allowed to cool to ambient temperature.

#### EXAMPLE XII

The following is a styling gel composition representative of the present invention.

Component	Weight %
Silicone Copolymer #7	2.00
Carbopol 940 <sup>1</sup>	0.75
Triethanolamine	1.00
Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> cross-linked polyacrylic acid, commercially available from B. F. Goodrich

This batch is made by mixing the listed components together in a conventional manner.

#### EXAMPLE XIII



The following is a hair mousse composition representative of the present invention.

Component	Weight %
Silicone Copolymer #7	3.00
Ethanol	15.00
Cocamine oxide	0.60
D.C. 190 <sup>1</sup>	0.20
Cocamide DEA	0.30
Perfume	0.10
Isobutane	7.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> dimethicone copolyol, commercially available from Dow Corning

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

#### EXAMPLE XIV

The following is a pump hair spray composition representative of the present invention.

Component	weight %
Silicone Copolymer #1	2.50
Dibutyl phthalate	0.20
Phenyldimethicone	0.30
Perfume	0.05
Aminomethyl propanol	0.20
Ethanol	q.s.

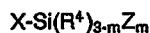
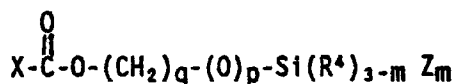
This composition is made by mixing the listed components together in a conventional manner.

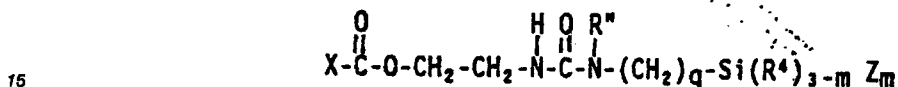
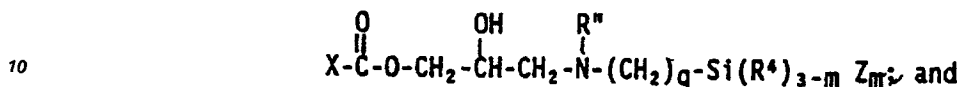
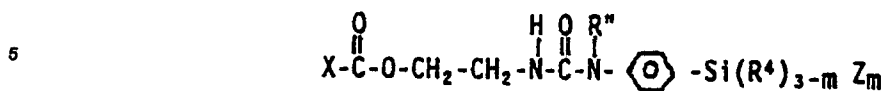
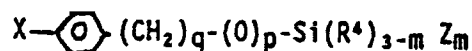
When the compositions defined in Examples I-XIV are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

#### Claims

1. A hair care composition characterized in that it comprises:

- (a) from 0.1% to 10.0% of a silicone-containing copolymer having a molecular weight of from 10,000 to 1,000,000 comprising a component selected from: a lipophilic low polarity free radically polymerizable vinyl monomer (A), a hydrophilic polar monomer which is copolymerizable with A (B), and mixtures thereof; together with a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000 preferably from 5,000 to 40,000, based on polydimethylsiloxane selected from

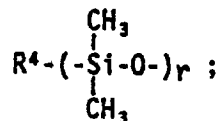




wherein m is 1, 2 or 3; p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is



R<sup>1</sup> is hydrogen or -COOH; R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH; Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700; and wherein the silicone-containing copolymer comprises from 0% to 98% monomer A, from 0% to 98% monomer B, and from 0.1% to 50% monomer C; and

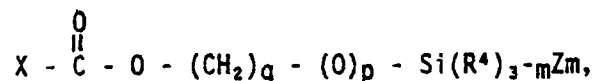
(b) from 0.5% to 99.5% of a carrier suitable for application to hair.

2. A hair care composition according to Claim 1 characterized in that the silicone-containing copolymer comprises from 5% to 98% monomer A, from 7.5% to 80% monomer B, and from 0.1% to 50% monomer C.

3. A hair care composition according to Claim 1 or 2 characterized in that monomer A is selected from acrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, aliphatic styrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

4. A hair care composition according to any of Claims 1-3 characterized in that monomer B is selected from acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaninoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof; and is preferably selected from acrylic acid, N,N-dimethylacrylamide, dimethylaninoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

5. A hair care composition according to any of Claim 1-4 characterized in that monomer C has the formula



- 5 preferably wherein  $p = 0$  and  $q = 3$ ,  $m$  is 1,  $r$  is about 250,  $R^4$  is alkyl,  $R^1$  is hydrogen, and  $R^2$  is methyl.
6. A hair care composition according to any of Claims 1-5 characterized in that the silicone-containing copolymer is selected from:
- acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 mw (10/70/20);
- N,N-dimethylacrylamide/isobutyl methacrylate/PDMS macromer -20,000 mw (20/60/20);
- 10 dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer - 20,000 mw (25/40/15/20);
- dimethylaminoethyl methacrylate/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);
- quaternized dimethylaminoethyl methacrylate/isobutyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);
- 15 acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);
- acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/10);
- N,N-dimethylacrylamide/methoxyethyl methacrylate/PDMS macromer -20,000 mw (60/25/15);
- dimethylacrylamide/PDMS macromer - 20,000 mw (80/20); and mixtures thereof.
7. A hair care composition according to any of Claims 1-6 characterized in that it is in the form of a
- 20 shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, which is preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.
8. A hair care composition according to any of Claims 1-6 characterized in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 20.0% of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof;
- 25 and from 0.05% to 5.0% of a cationic surfactant, preferably a quaternary ammonium surfactant.
9. A hair care composition according to any of Claims 1-6 characterized in that it is in a form selected from hair sprays, mousses, hair tonics and gels.
10. A method of conditioning and styling hair characterized in that it comprises applying to the hair an effective amount of the composition according to any of Claims 1-9.

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# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 8391

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 834 972 (ALLIED-SIGNAL INC.) * Column 1, line 40 - column 2, line 27 *	1-10	A 61 K 7/06 A 61 K 7/48
A	--- CHEMICAL ABSTRACTS, vol. 88, 1978, page 271, abstract no. 54975g, Columbus, Ohio, US; & JP-A-77 57 337 (MATSUSHITA ELECTRIC WORKS, LTD) 11-05-1977 * Abstract *	1-10	
A,D	--- US-A-4 136 250 (CIBA-GEIGY CO.) * Claims 1-17 *	1-10	
A,D	--- US-A-4 728 571 (MINNESOTA MINING & MANUFACTURING CO.) * Claims 1-14 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 61 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-11-1990	Examiner BERTOCCHI C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	